PRECIPITATION SAMPLER COMPARATIVE STUDY

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Acidic Precipitation in Ontario Study

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PRECIPITATION SAMPLER COMPARATIVE STUDY

A Study Carried Out for

The Ontario Ministry of the Environment

Air Resources Branch

BY

Concord Scientific Corporation

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and

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TABLE OF CONTENTS

SUMMARY

A three month experimental study to evaluate the relative performance of three different designs of "event" rain samplers was carried out beginning in August 1979. The samplers evaluated were an automatic, "wet only" type (Aerochem Metrics); a funnel and bottle type; and an especially fabricated polyethylene bag inserted in a large mouth plastic bucket.

Each sampler was run in duplicate and operated in a "24-hour event" mode; that is, on days for which precipitation was forecast, the samplers were placed in the field at 0930 hours and were collected 24 hours later. The quantity and pH of the collected samples were determined immediately upon return to the laboratory with the remainder of the sample being stored in polyethylene bottles at 4° C until chemical analysis could be performed. The samples were, in addition to pH and quantity, analyzed routinely for SO_4^{-2}, NO_3^-, NH_4^+, Cl^-, Ca^{+2}, Mg^{+2}, Na^+, K^+, and F^-, and conductivity along with NO_2^-, PO_4^{-3}, Br^-, SO_3^{-2}, however, these latter four were virtually always below the limit of detection. Also, at the field site, wind speed and direction were monitored at the 10 m level with a 45 B anemometer, and precipitation amount was measured with a Tipping Bucket rain gauge. Operating concurrently at the site was an Air Resources Branch/Ministry of the Environment (ARB/MOE) monthly, wet only (Sangamo) sampler.

Based upon the above measurements, overall sampler performance was assessed in terms of susceptibility to contamination, catch efficiency,

mechanical reliability and sampler reproducibility. A comparison was also made between the monthly, wet only aggregate data and the summed event data.

CONCLUSIONS

The conclusions of this investigation may be summarized as follows:

- Overall, the Aerochem Metrics (A) sampler, of the three designs tested, would yield the best results under a greater variety of ambient conditions; however, for certain parameters and many events, the Sudbury Event Sampler (S) would yield virtually identical data.
- Using the data from all the events, the Funnel and Bottle (F) and Sudbury Event (S) type samplers yielded significantly different (95% confidence) results from an automatic wet only type sampler for a number of parameters including: Ca^{+2}, Mg^{+2}, SO_4^{-2}, NO_3^-, H^+, K^+. Thus, for these rain constituents (at least at this site), the use of F and S samples in the 24-hour event mode is unsatisfactory for all of the observed events.
- The F and S samplers, run in the 24-hour event mode, yielded results for NH_4^+, conductivity and rainfall recovery which are not significantly different from those obtained with the automatic, wet only sampler and thus could be used for these parameters (at this site at least).

- The S sampler generally gave results that were in slightly better agreement with the automatic wet only sampler than those obtained with the F sampler.
- The S sampler was the easiest of the three designs examined to use and also was found to be the most maintenance free.
- The H^+ was found to correlate most strongly with SO_4^{-2}, NO_3^-, and NH_4^+ for events where the rainfall $\geq$ 2.8 mm.
- The Aerochem Metrics and the Sangamo samplers have a rain catch efficiency very close to that of the Tipping Bucket rain gauge.
- The division of the complete data set into sub-sets according to rainfall amount and a contamination index composed of wind speed and length of dry period reduced the variance between the A and the F & S samplers for H^+ to insignificance, and did likewise for Ca^{+2} and SO_4^{-2} for the A & S samplers.
- For sampling days for which the rainfall was less than 2.8 mm or the sampling day was generally windier and drier (average wind speed during the dry periods x fraction of the sampling day which was dry > 11 km/hr.), there was distinct evidence of dry contamination of the samples from all three sampler types.
- Results obtained with an automatic, monthly, wet only sampler are different from those obtained by summing the results obtained with the event samples for the two months for which complete data are available.
- The F and S samplers have a greater catch efficiency than the Tipping Bucket rain gauge.
- The differences observed between the results obtained with either the F or S sampler and the A sampler are due to dry contamination.

- Evaporation did not appear to be a significant problem with either the F or S sampler in this study.

RECOMMENDATIONS

Based upon the findings of this investigation, it is recommended that:

- for event studies of rain chemistry, an automatic wet only type (such as the Aerochem Metrics) sampler be used and the use of samplers such as the funnel and bottle and the Sudbury event be discontinued, unless the conditions which would yield equivalent data with the "open" samplers have been established at that site.
- a comprehensive investigation of the relationship between monthly vs summed event results be carried out as soon as possible to determine if the observed differences are a significant phenomenon.
- all monthly, wet only data be treated with appropriate caution until the above recommended study is complete.
- even data obtained with wet only samplers operated in the "24-hour event" mode be viewed as subject to some dry contamination for drier and windier sampling days or those with light rainfall (less than $\sim$ 3 mm).
- where possible and practical, wet only samplers be used strictly in an event mode at sites of light rainfall, or those subject to higher winds during dry periods or other conditions which would favour dry contamination.

I. INTRODUCTION

Up until relatively recently, circa the early 1979's, the sampling of precipitation for chemical analysis was thought to be a rather simple matter, and consequently, it was common that rather simple approaches were used. This included a variety of designs of open containers, constructed of a number of materials, and these were left out at the sampling sites for varying periods, typically the order of a month. In the early 1970's, a number of investigators became concerned about this type of approach and several studies were conducted (1 - 6) to compare the performance of different precipitation sampler designs and sampling methodologies. These studies have yielded a number of important conclusions, principally the following:

- The ratio of monthly bulk deposition to monthly wet deposition is significantly greater than 1.0 for several parameters, e.g. Ca^{+2}, Mg^{+2}, Na^{+} and K^{+}.
- Results obtained from composite samples obtained with a sampling period greater than one week can be very different from those obtained by summing the amounts in individual storm samples over the sampling periods.
- Of the samplers tested, the Hubbard Brook (Funnel and plastic bottle) and the Health and Safety Laboratory (HASL) of the U. S. DOE type have been found to be, generally speaking, the most satisfactory samplers.
- All the automated samplers perform rather unsatisfactorily during rain-freezing rain-snow episodes.

- Standard rain and snow gauges are necessary to determine the quantity of precipitation that has fallen.
- The time of storage of samples should be minimized; however, for most parameters, storage for several months at 4°C in sealed plastic containers has proved satisfactory, provided the pH $\leq$ 4.5.
- Wind shields do not consistently improve the collection efficiency of a precipitation collector relative to a standard rain gauge.
- Evaporation can be a serious problem with a number of samplers.
- The automatic samplers are rather poor regarding snow collection efficiency.
- For snow collection, the sampler height to diameter ratio appears to play an important role in collection efficiency.

The above list is not meant to be exhaustive but rather to serve as a synopsis of the previously obtained information relevant to the work described in this report.

The data available to date infer that an automatic wet only type sampler operated in an event mode would satisfactorily minimize the dry deposition of other contaminant contributions to a collected rain sample, and thus provide reliable data upon which meaningful interpretations could be made. However, the relatively high cost ($\sim$ \$2K capital, several hundred dollars installation plus maintenance costs) makes the use of this type of sampler for an event network of

any appreciable size somewhat unattractive financially. Also, this type of collector could well be unsuitable for snow as the catch efficiency is variable and usually low.

Thus, if a satisfactory, inexpensive, alternative could be found, it would represent a major step forward in event precipitation sampling. It was with this in mind that the ARB of MOE developed the S sampler. However, because of the wide mouth of the collector, and the fact that it is open for a full 24-hour period with the possibility of dry periods in this interval, leads to some unease about the possibility of sample contamination.

Another design that has been sometimes used is the (F) design. It was felt that this design could afford a relatively large collection area and at the same time, offer a relatively small area for dry deposition or other contamination, and given the rather short time the sampler was in the field, might be a suitable alternative to the more costly automatic samplers or the S sampler.

To assist in the selection of a satisfactory sampler, a comparative study of three types of samplers, operated in a "24-hour event" mode, was carried out for the Ontario Ministry of the Environment from mid-August to the end of November 1979, with a total of 32 events being sampled. The three sampler types studied were an automatic, wet only type (A) manufactured by Aerochem Metrics Inc.; a funnel and bottle sampler; and an "ARB/SES event sampler".

II. EXPERIMENTAL

II-A. Site and Equipment

The site for this investigation was the Atmospheric Environment Service's Experimental Station in Woodbridge, Ontario. A rough map showing the study site location is given in Fig. II-1. This site was well equipped, having in addition to the equipment used for this study, a variety of instruments including: a Fisher-Porter rain-gauge, a Tipping Bucket rain gauge, a meteorological tower which provided wind speed data at 10 m, 1 ARB/MOE Sangamo rain sampler, 1 CCIW Sangamo sampler, 2 CCIW Bulk samplers, and a MOE-ARB storage gauge.

This site has a number of unique characteristics which should be borne in mind when evaluating the results obtained during this study and particularly when considering their applicability to other sites.

The sampling instruments used in this study were two Aerochem Metrics rain samplers (A), two funnel and bottle samplers (F) and two Sudbury Environment Study event samplers (S) and two strip chart recorders to record the open/closed cycle of the Aerochem Metrics sampler.

Photos of the samplers are shown in Fig. II-2, with sketches and dimensions for the A, F & S samplers given in Fig. II-3. The actual sampler arrangement used is illustrated in Fig. II-4.

II-B. Sampling Procedure

At approximately 0830 hours, an assessment by MEP Company meteorologists was made of the probability of precipitation occurring that day. If the probability was greater than 25%, then carefully cleaned (de-ionized H_2O washed) sample containers were transported to the site in clean plastic bags and installed in the samplers. The installation was usually complete by 0930 hours. The samples were picked up at 0930 hours the following day, and, if rain was forecast for that day as well, a new set of containers were installed in the rain samplers. The collected samples were transported immediately to the laboratory and the pH and sample volume were determined as soon as possible (typically ½ hour) after pick-up. The samples were then stored in polyethylene bottles at approximately 4°C until analysis. The storage time before analysis varied from one week to about two months.

II-C. Analytical Procedures

Initially, analysis of the samples for pH, SO_4^{-2}, NO_3^-, Br^-, Cl^-, NH_4^+, F^-, SO_3^{-2}, NO_2^-, PO_4^{-3}, Na^+, K^+, Mg^{+2}, Ca^{+2} and conductivity was attempted, but experience showed that for these samples, the concentrations of Br^-, SO_3^{-2}, NO_2^-, PO_4^{-3} were so low that they would be totally masked by the presence of the much more dominant ions (e.g. SO_4^{-2}, NO_3^-) in the chromatogram. Ion concentrations were determined by a Dionex Model ion chromatograph and pH was determined using a Radiometer model pH meter.

The chromatographic conditions for the anion analysis were as follows:

3 x 500 mm Separator Column

6 x 250 mm Supressor Column

0.003 M $NaHCO_3$/0.0024 M Na_2CO_3 Eluent

35% Flow

3 μ Siemen Scale

Using these conditions, the reproducibility of peak heights and retention times was good. A chromatogram of a prepared sample is given in Fig. II-5. A summary of relevant parameters is given in Table II-1.

Table II-1

Anion	Retention Time ± 0.1 min.	Calibrated Range mg/1	Limit of Detection mg/1
F^-	1.0	0.00 - 0.25	0.01
Cl^-	2.9	0.00 - 2.00	0.02
NO_2^-	3.5	0.00 - 0.40	0.01
PO_4^{-3}	5.0	0.00 - 0.40	0.08
Br^-	6.3	0.00 - 2.50	0.10
NO_3^-	7.2	0.00 - 5.00	0.10
SO_4^{-2}	10.3	0.00 -10.00	0.10

The conditions for the monovalent cation analysis were:

6 x 250 mm Separator Column

3 x 250 mm Supressor Column

0.005 N Ultrex HNO_3 Eluent

50% Flow

3 μ Siemen Scale

Good sensitivity and peak height and retention time reproducibility were obtained with these conditions and a summary of relevant parameters is given in Table II-2:

Table II-2

Cation	Retention Time ± .1 min.	Calibrated Range mg/l	Error mg/l	Limit of Detection mg/l
Na^+	5.0	0.00 - 1.00	0.01	0.02
NH_4^+	6.3	0.00 - 2.00	0.03	0.03
K^+	7.5	0.00 - 0.50	0.01	0.05

For the divalent cations, the analytical conditions were:

6 x 250 mm Separator Column

3 x 250 mm Supressor Column

0.0025 M meta-phenylene diamine.2HCl/0.0025 N Ultrex HNO_3 Eluent

50% Flow

3 μ Siemen Scale

As with the other ions, good sensitivity, retention time and peak height reproducibility were obtained with these conditions and a summary of pertinent parameters is given in Table II-3.

Table II-3

Cation	Retention Time ± 0.1 min.	Calibrated Range mg/l	Error mg/l	Limit of Detection mg/l
Mg^{+2}	4.0	0.00 - 1.00	0.01	0.02
Ca^{+2}	6.3	0.00 - 5.00	0.02	0.06

A laboratory intercomparison study of analytical methods was carried out with the Water Quality Section of the Ontario Ministry of the Environment. Twenty (20) actual rain samples and ten (10) prepared solutions were used in the intercomparison, and the results were analyzed statistically using the paired "t-test". There was no significant difference (95% confidence level) between the UTS and MOE results with the exception of Mg^{+2}, for which there was a constant difference of about 30% in the results. This was subsequently traced to an incorrectly labelled calibration solution at UTS and the results for Mg^{+2} were adjusted accordingly.

The conductivity measurements were made at the Water Quality Section laboratories of MOE. Calibration was carried out with KCl solutions and the measurements made at 25.5°C.

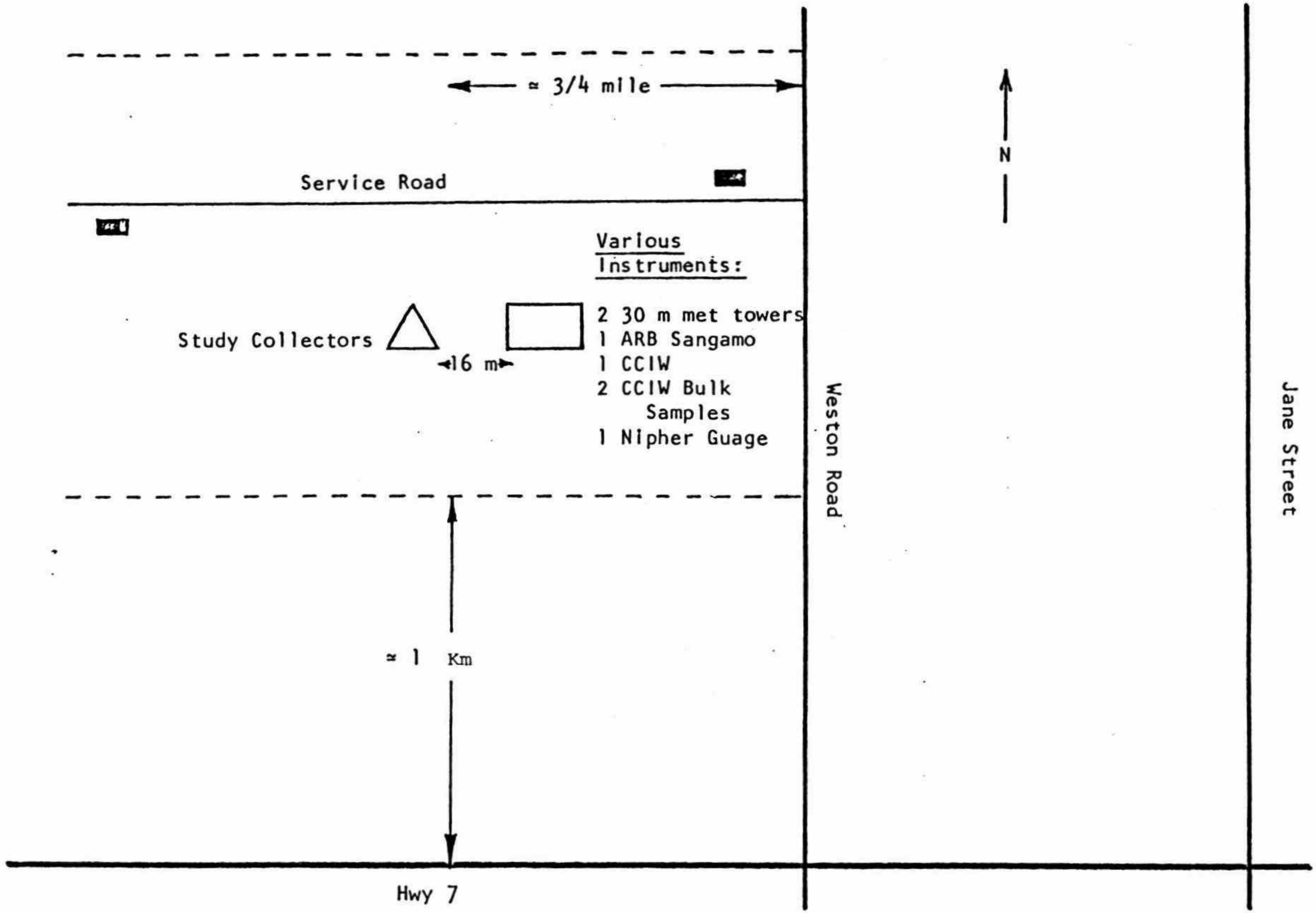


Figure II-1 Schematic Diagram of Woodbridge AES Experimental Station

Fig. II-2

Sampler Photos

Fig. II-2

Figure II-3a

Aerochem Metrics Sampler

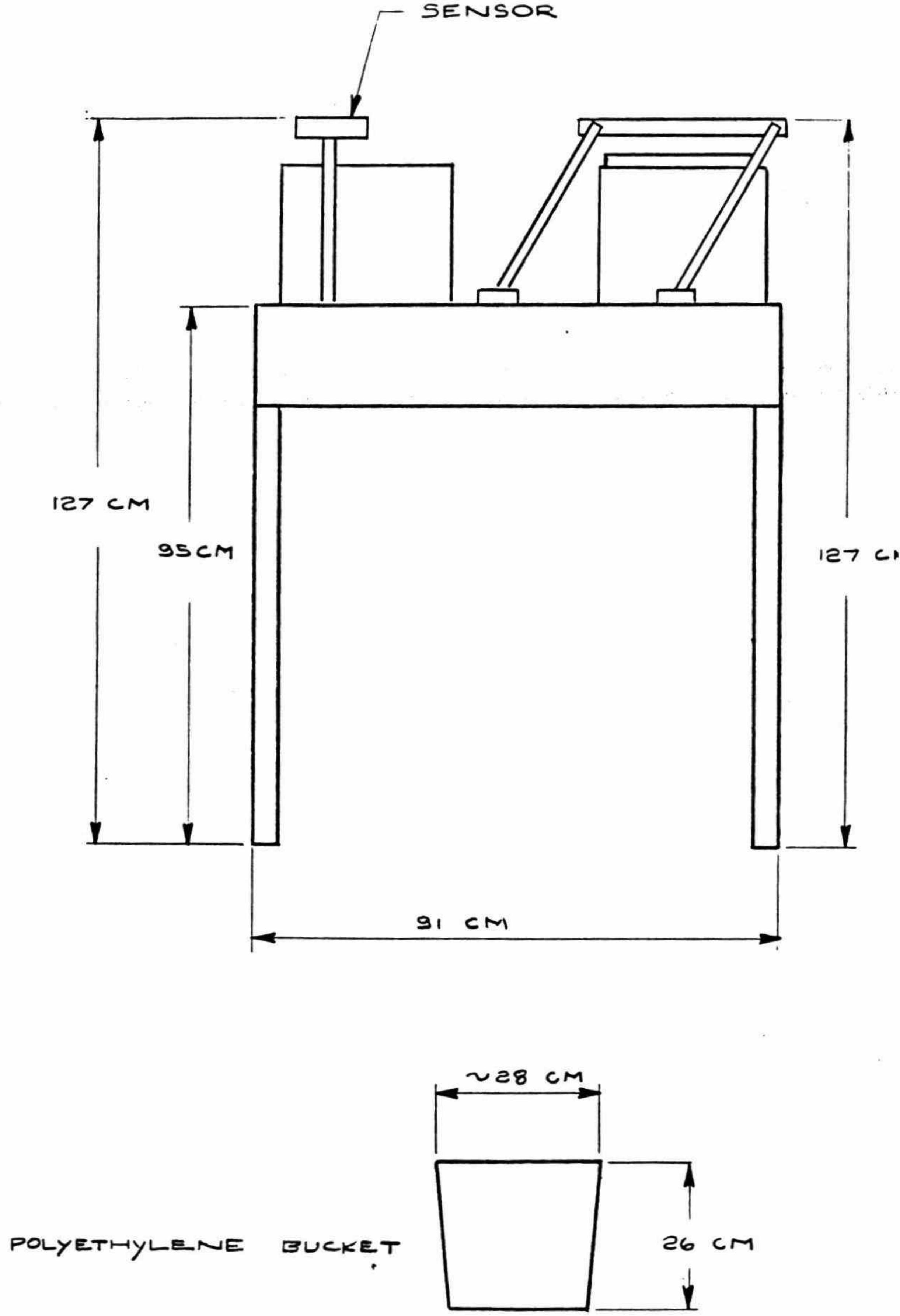


Figure II-3b

Funnel And Bottle Sampler

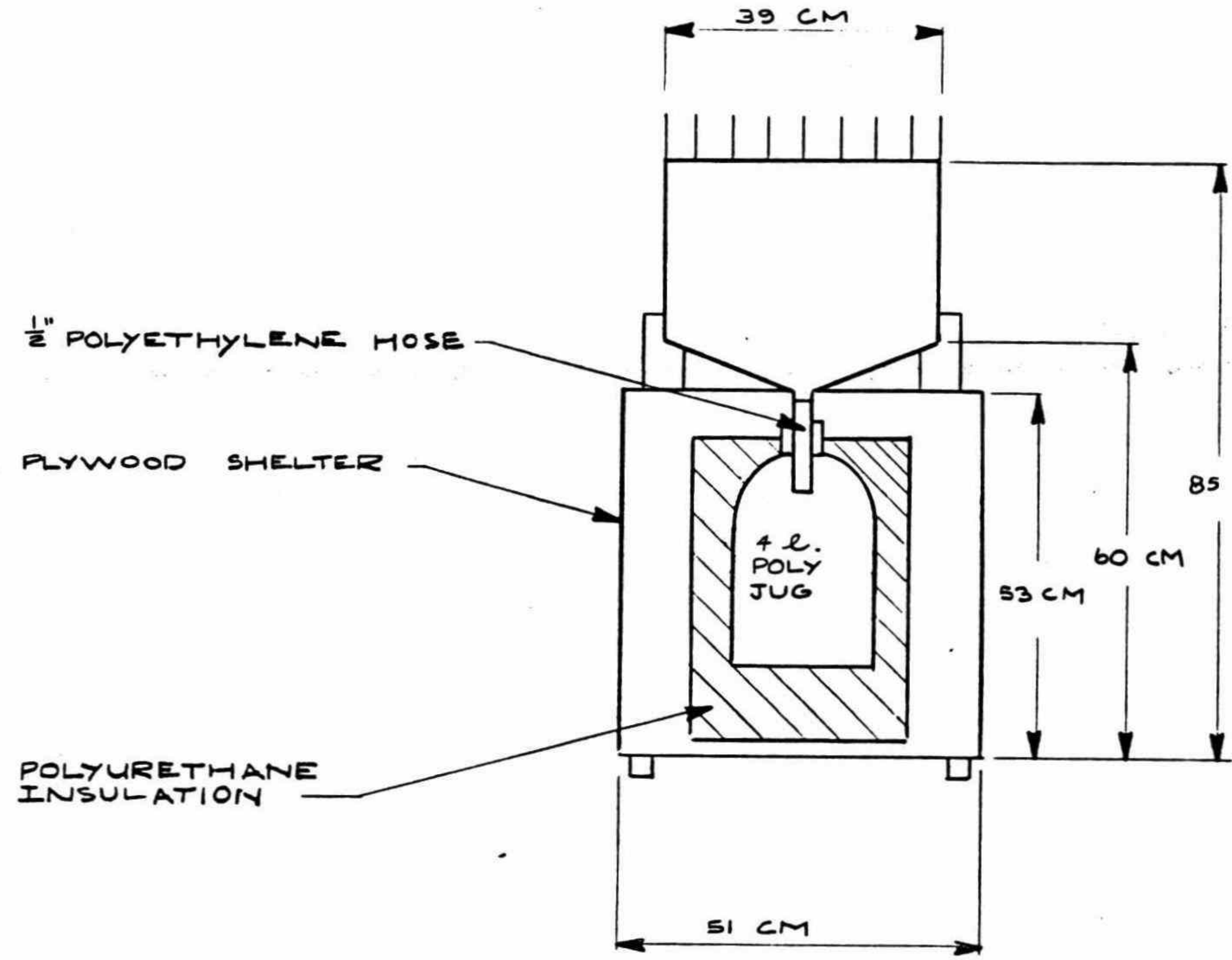
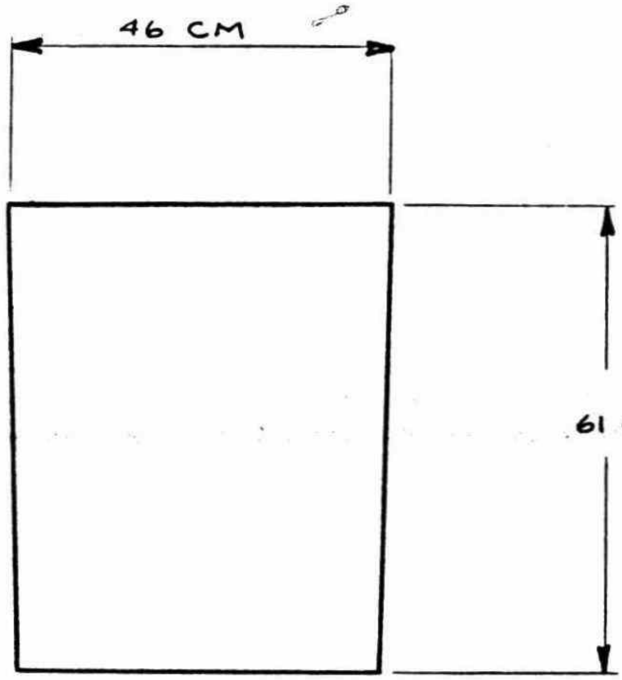


Figure II-3c

Sudbury Event Sampler



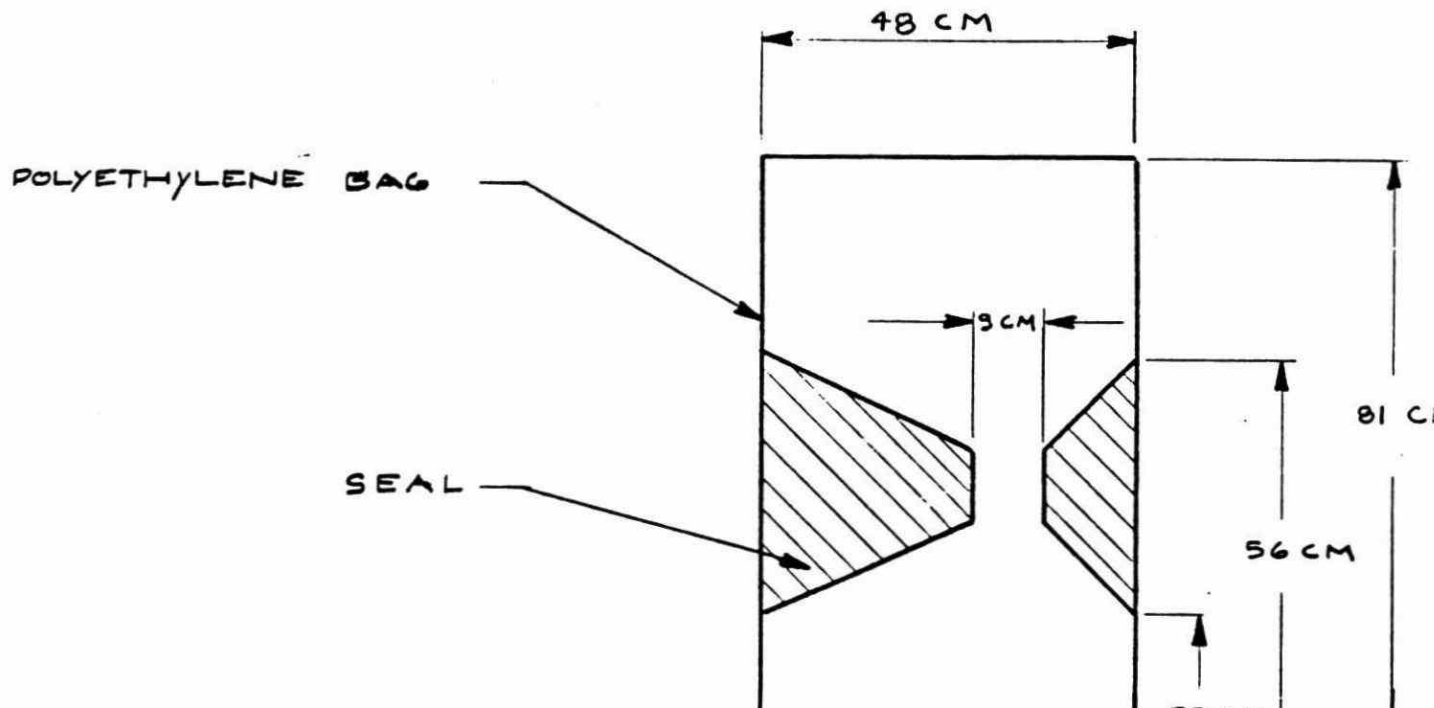


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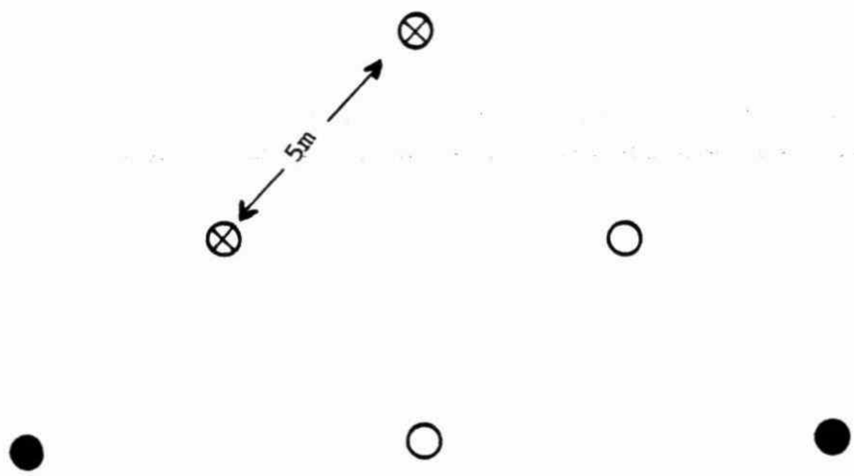
Figure II-4

Sampler Arrangement

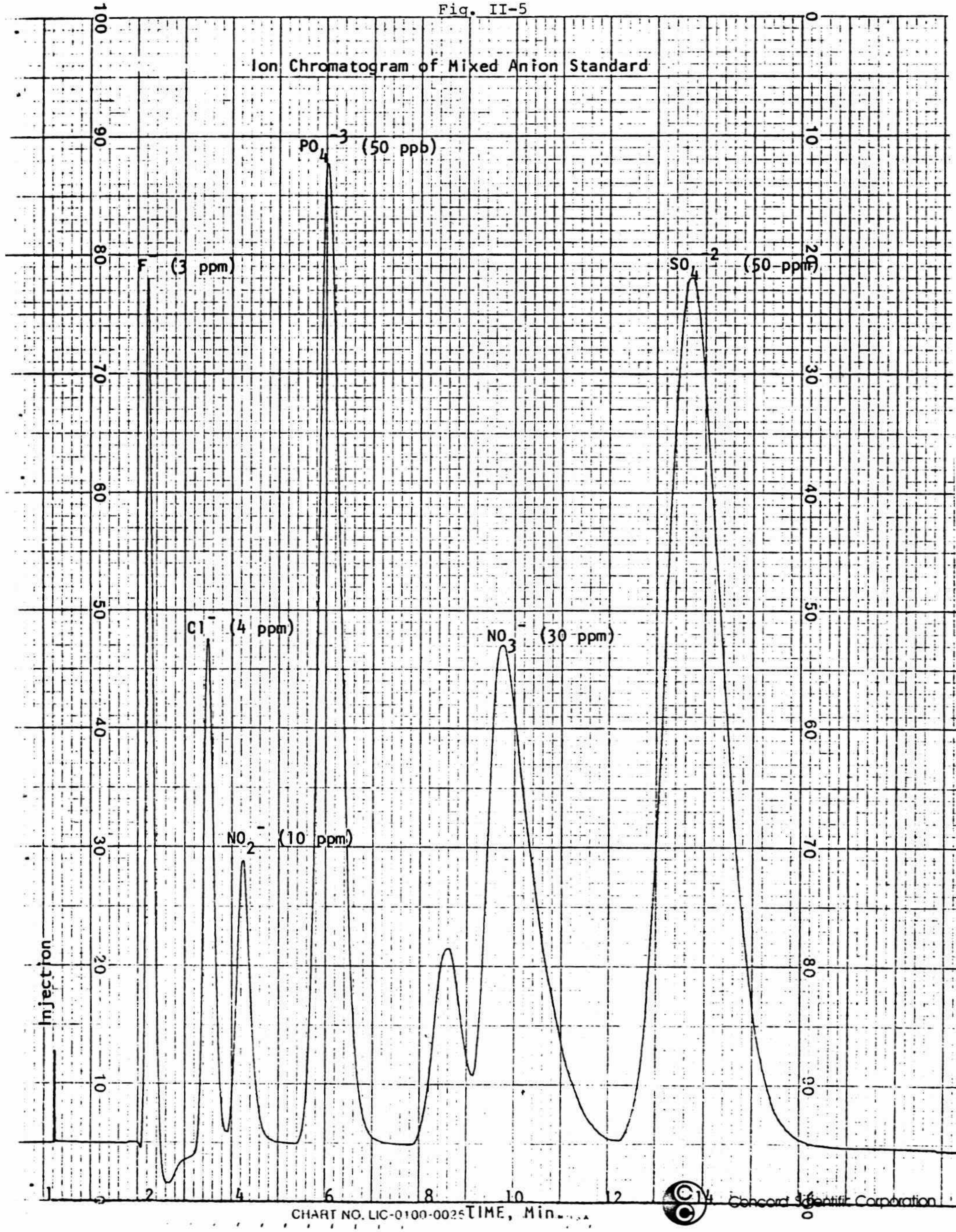


Aerochem Metrics Collector

Funnel And Bottle Collector

Sudbury Environmental Study Event Collector

Fig. II-5


Ion Chromatogram of Mixed Anion Standard
F⁻ (3 ppm)
Cl⁻ (4 ppm)
NO₂⁻ (10 ppm)
PO₄⁻³ (50 ppb)
NO₃⁻ (30 ppm)
SO₄⁻² (50 ppm)
Injection
TIME, Min.
CHART NO. LIC-0100-0025
Concord Scientific Corporation

III. RESULTS AND DISCUSSION

III-A. Event Sampler Comparisons

A summary of the conditions which prevailed during the study is given in Table III-1. A parameter concentration - event matrix was prepared for each of the measurable parameters of interest. These matrices are given in Appendix A. The concentration data were subjected to the standard paired "t-test" to examine the variance for a given sampler type ("within sampler type") for each constituent and subsequently for the variance between sampler types for each constituent. The within sampler type and between sampler type comparison are given in Tables III-2 and III-3 respectively.

An examination of Table III-2 will reveal that, at the 95% confidence level, there is no significant variation in the results obtained by two samplers of the same type for any parameter except for rainfall amount as measured by the funnel and bottle (F) sampler, and for H^+ for the S sampler. These results are rather surprising, and it was felt that the reason might become apparent on re-examining the within sampler variances as a function of quantity of rainfall (R), in mm, and as a function of the product of the fraction of the day which was dry times the average wind speed during the dry period. As can be seen from Tables C1 - C10 in Appendix C, the difference in H_3O^+ concentration in adjacent S samplers and rainfall amount in the F samplers is significant for days of heavier rainfall ($R \geq 2.8$ mm & $R \geq 5.0$ mm) and for the damper

and calmer sampling days ($\overline{U}.f \leq 11$ km/hr.), where "$\overline{U}$" is the average wind speed, in km/hr, during the dry portion of the sampling period and "f" is the fraction of the sampling period which was dry.

The rainfall amount R = 2.8 mm was chosen as a cut point as it is the median for this data set. The value R = 5.0 mm was chosen to see if the between sampler differences would be even further reduced for these heavier events. The use of an even larger rainfall amount (e.g. R = 7 mm) as the cut point was precluded by an insufficient number of heavier events during the study period. The reason for the significant difference in R for the heavier events is quite possibly related to spillage of some of the sample during the sample gathering operation as due to the design of the sampler, sample removal under these circumstances would require somewhat more care. The reason why the between sampler (H_3O^+) variance is significant for adjacent S samplers during heavier events is more difficult to rationalize and is not, at this time, at all clear.

As it was felt that the Aerochem Metrics (A) sampler would best eliminate extraneous contamination of the three sampler types examined and thus give the "truest" results, the data from the other two sampler types funnel and bottle (F) and Sudbury Event Sampler (S) were compared to those from the A sampler for the between sampler type comparisons.

Consideration of Table III-3 will show that the F & S samplers' performance was quite similar, with the S sampler being slightly better. Not surprisingly, both the F and S samplers showed significant differences from the A sampler for a number of "soil related" parameters, such as K^+, Ca^{+2}, Mg^{+2}, as well as for a number of "non-soil related" parameters such as H^+, SO_4^{-2}, NO_3^-. There were no significant differences found between the samplers for NH_4^+, conductivity and rainfall amount. As mentioned earlier, the S sampler gave slightly better results in that the results obtained for Na^+ and F^- were significantly different from those obtained with the A sampler at the 90% confidence level but not at the 95% level.

The observed differences between the samplers obtained with the A and the S and F samplers for K^+, Ca^{+2}, and Mg^{+2} are almost certainly due to dry contamination. The effect of this dry contamination on the H^+ concentration would depend upon whether the contaminating compound was a base or acid anhydride (e.g. $MgCO_3$ vs $MgSO_4$). Also, a contaminating compound containing SO_4^{-2}, such as $MgSO_4$, would also affect the SO_4^{-2} concentration.

Another source of difference between the SO_4^{-2} concentration measured with the A and the F & S samplers would be the dry deposition (atmospheric absorption) of SO_2 with its subsequent oxidation to SO_4^{-2}. It is worth noting that the ratio plot (Appendix B) for $SO_4^=$ in the A sampler vs that found in the F & S sampler is similar to those obtained by Galloway and Likens (3). These authors, unfortunately, did not

report a statistical analysis of their data; however, given that their ratio plots closely resemble those obtained in this study, it is very likely that their results for the comparison between open and wet only samplers were statistically significant as well.

The difference in the NO_3^- concentration observed in the A and F & S samplers very likely is affected by the high vapour pressure of HNO_3 (the equilibrium vapour pressure of HNO_3 above solution such as those found in precipitation samples is several hundred parts per billion)[8], and also by the fact that several of the soil derived metals exist as nitrates (e.g. KNO_3).

It should be remembered that the observed concentrations of the various precipitation constituents are the cumulative result of two processes: precipitation scavenging (rainout and washout) and dry contamination. If precipitation scavenging is the dominant mechanism, (i.e. dry contamination is insignificant) then there should be no difference in the results obtained with two adjacent samplers, provided the capture efficiency of the two samplers is the same and cleaning and handling procedures are equivalent. Thus, if there is a significant difference between sampler types for a given constituent, then dry contamination is making a significant contribution, for this constituent. Since it is apparent (see Table III-3) that dry contamination is significant for a number of parameters, it was decided to statistically re-analyze the data sets, which were sub-divided according to rainfall amount and dry period-wind speed as before, to see if the statistics improved during conditions which minimize dry contamination.

The results, as mentioned earlier in this section, are given in Tables C 1 to C 10 in Appendix C. Except for R in the F sampler and H_3O^+ in the S sampler as discussed earlier, the within sampler type variance is insignificant for each sampler and constituent under all conditions. Thus, there is no change from the whole data set.

For the between sampler type variances, however, the sub-division of the data does result in some changes. For example, for $R \geq 2.8$ mm (Table C2), the variance between the A & F and A & S samplers for H_3O^+ becomes insignificant. Also, for SO_4^{-2} and Ca^{+2}, the variance between the A and S samplers also becomes insignificant. Raising the cut point to R = 5.0 mm, further reduces the between sampler variance. For example, for events with R > 5.0 mm, the paired t-test values for between sampler variance are further reduced from those obtained for events with $R \geqslant 2.8$ mm. In fact, the between sampler variance between the A & F samplers is not significant for Cl^-, F^- and NO_3^- for events with R > 5.0 mm. A similar result is obtained for the data for which $\overline{U}.f \leq 11$ km/hr (Table C6). These observations suggest the following:

- that for sampling days where $R \geq 2.8$ mm and $\overline{U}.f \leq 11$ km/hr, there would not be a significant difference between the results obtained with the A & S samplers for H_3O^+, SO_4^{-2} and Ca^{+2} in addition to those parameters which showed insignificant differences for the whole data set.

- for sampling days where R > 5.0 mm, there would not be a significant difference between the results obtained with the A & F samples for Cl^-, F^-, and NO_3^- in addition to those parameters which showed insignificant differences for events with $R \geq 2.8$ mm.

- that so sub-dividing the data set does indeed reduce the effect of dry contamination. If precipitation scavenging were the dominant mechanism contributing to the various constituent concentrations then the sub-division of the data set should not have a significant effect.

Another point worth mentioning is that there is no significant difference between sampler types observed for NH_4^+. This suggests that precipitation scavenging and not dry contamination is the dominant contributory factor to the observed precipitation concentrations for this parameter.

The ratio of the H^+ concentration in the F sampler to that in the A sampler (Fav/Aav) as well as (Sav/Aav) for each event is given in Table III-4. As can be seen from Table III-4, the H^+ concentration in the F or S sampler is, on average, 85% that found in the A sampler, if all events are included. However, if one or two "outliers" are

omitted, then the ratio drops substantially. Also, it should be noted that for the F sampler the ratio varied from 0.097 to 3.9 whilst the ratio for the S sampler varied from 0.015 to 2.9. In view of this very broad variation, it would be very unwise to use average values to relate (H^+) found in a F or S sampler to that which would be found in an A sampler, as the result could be very misleading, as the ratio observed for actual events can be very different from the average value.

To illustrate the parameter ratios graphically, concentration ratio plots for each parameter were prepared and can be found in Appendix B. As would be expected after review of Table III-3, the ratios vary substantially from 1.0 and are particularly bad for the soil related elements Ca^{+2} and Mg^{+2} as well as Na^+ and K^+, for which the observed concentrations were often near the detection limit in the A sampler, and thus, only a small amount of contamination would be required to make the ratio much greater than 1.0.

III-B Parameter Correlation Co-efficients (r)

Tables III-5, 6, 7 are the parameter correlation co-efficient matrices for the A, F and S samplers respectively for all events. It should be remembered that for this study, the Aerochem Metrics samplers, because of its design, would yield the most contamination free data, assuming they operated correctly.

It should be borne in mind that the degree of confidence that one can put in correlation co-efficients between two variables increases with the number of observations. Consequently, the error limits for "r" values obtained with data from all the rain events are smaller than those for "r" values from one of the sub-divided data sets. As a guide, the implications of the "r" values can be catagorized as follows:

"r" Value	Implication
≥ 0.75	Strong correlation
$0.5 \leq r \leq 0.75$	Moderate correlation
$0.25 \leq r \leq 0.5$	Weak correlation
< 0.25	Low correlation

Reference to Table III-5 reveals some expected and some surprising results. For example, the correlation co-efficients between H^+, $SO_4^=$ and NO_3^- are significant as is r for Mg^{+2} and Ca^{+2} as well as that between Na and Cl^- and Ca^{+2}.

Somewhat surprising is the fact that Ca^{+2} correlated rather well with $SO_4^=$ and that NH_4^+ correlated more poorly with H^+, NO_3^- and $SO_4^=$ than would be expected. An examination of Tables III-6 and III-7 clearly shows that the correlation matrices for the F & S samplers are very different from that of the A sampler. The r values contained in Tables III-6 and -7 suggest the effect of dry deposition in the F & S samplers. This can be seen from the fact that H^+ and SO_4^{-2} correlate moderately well for the A sampler (Table III-5) but correlate much more poorly with the F (Table III-6) and S (Table III-7) samplers. Also NO_3^- and SO_4^{-2} correlate better with Ca^{+2} and Mg^{+2} for the F and S samplers than

they do for the A sampler. Thus, even when used in the 24-hour event mode, it is not possible to use data from F & S type samplers to obtain correlation co-efficients that are equivalent to those derived with "wet-only" data.

In an attempt to see if there were some atmospheric conditions under which the matrices obtained with the different samplers were more similar, the complete set of all events was sub-divided into subsets according to the criteria used previously viz:

- events with rainfall $\geq$ 2.8 mm ($n \cong 12$)
- events with rainfall $\leq$ 2.8 mm ($n \cong 10$)
- events where the product of the average wind speed during the dry period times the fraction of the sampling period which was dry (i.e. $\bar{U}$. f was < 11 km/hr ($n \cong 10$)
- events where the product $\bar{U}$. f $\geq$ 11 km/hr ($n \cong 10$)

The subsets with rainfall (R) $\geq$ 2.8 mm and $\bar{U}$. f $\leq$ 11 km/hr. would be events for which dry contamination would be minimized whereas it would be greater for events for which R < 2.8 mm or $\bar{U}$. f > 11 km/hr. (See Section III-A). Also, use of the product $\bar{U}$. f should help separate the rain samples not only in a way that would minimize dry deposition/contamination but evaporation as well.

The r matrices for these conditions (R $\geq$ 2.8 mm or $\bar{U}$. f $\leq$ 11 km/hr) are given in Tables III-8 to III-13. As can be readily seen by examination of these tables, the effect of sub-dividing the data set is striking.

For example, the r values between H^+, $SO_4^=$, NO_3^- and NH_4^+ improve significantly, particularly for the F & S samplers. The correlations are very slightly better for the set with $\overline{U}$. f $\leq$ 11 km/hr compared with those obtained with R $\geq$ 2.8 mm. It can also be noted that the r value between Ca^{+2} and Mg^{+2} is very high, particularly for the A sampler with events $\overline{U}$. f $\leq$ 11 km/hr. Also for the A sampler, the correlation between Na^+ and Cl^- and Ca^{+2} for all events disappears for events with R $\geq$ 2.8 mm and those were $\overline{U}$. f $\leq$ 11 km/hr. Also, moderate correlation is observed between NO^{-3} and F^- for both data subsets. The reason for this is not readily clear.

Examination of Tables III-14 and III-15 (events with R < 2.8 and $\overline{U}$. f < 11 km/hr for the A sampler respectively) reveals another interesting finding, i.e. the correlation co-efficients between H^+, $SO_4^=$, NO_3^- and NH_4^+ have degraded markedly. Also the correlation between soil derived parameters (e.g. Na^+, Ca^{+2}, Mg^+) and SO_4^{-2} and in some cases NO_3^-, Cl^- and F^- has increased sharply, when compared to that obtained with the A sampler for events with R $\geq$ 2.8 mm or $\overline{U}$. f $\leq$ 11 km/hr. This suggests that possibly even with the A sampler operated in a "24-hour event mode", dry deposition/contamination can be serious, under certain atmospheric conditions, and thus in these instances, one is not necessarily measuring only rain quality but a complex combination of rain quality, dry deposition/contamination and evaporation.

The correlations between H^+, SO_4^{-2}, NO_3^- and NH_4^+ are even further degraded with the F & S samplers for these events (R < 2.8 mm and $\overline{U}$. f > 11 km/hr). Examination of these matrices (Tables III-16, 17, 18, 19) readily reveals the suggestive evidence of dry contamination.

Therefore, the foregoing discussion suggests the possibility that for the above conditions ($R < 2.8$ mm $\overline{U}$. $f > 11$ km/hr), none of the tested samplers, used in the "24-hour event" mode, is adequate, at least at this site.

III-C Rainfall Capture Efficiency

In Table III-20, the summed event rainfall recovery data for the A sampler are compared with the Sangamo (So) sampler and the Tipping Bucket (TB) rain gauge. As can be seen from Table III-20, the catch efficiency for the A and So samplers is virtually identical, and each is approximately 8 - 10% more efficient than the TB gauge. It should be noted that in Table III-20, the rainfall measured by the Tipping Bucket gauge for September and November is calculated with data that correspond to the sampling days with the A sampler.

III-D Summed Event vs Monthly Wet Only Samples

In addition to the within sampler and between sampler type comparisons it was considered of importance to compare the concentration data obtained with a monthly, wet only sampler to those obtained by calculating the volume weighted average concentrations from all the events occurring during that month. In this report, these will be referred to as monthly vs summed event data for simplicity's sake.

The Air Resources Branch of the Ontario Ministry of the Environment had in operation at this site during the study period a wet only sampler, which collected rain for a month before the collection bucket was replaced. The data obtained from this sampler are given in Table III-21.

For comparative purposes, the volume weighted average parameter concentrations obtained with an "Aerochem Metrics" sampler operated in a "24-hour event" mode were computed and given in Table III-22 along with the monthly data and the ratio of summed event to monthly data.

The results in Table III-22 contain several significant aspects; however, it should be noted that complete event data are available only for September and October. It is also noteworthy that September 1979 was a drier month than normal (see Table III-23) while October 1979 was wetter than normal [7].

As can be seen from Table III-22, the ratio of the summed event data to the monthly wet only data is less than one for every parameter except Cl^- for both September and October. This is particularly so for Ca^{+2} and Mg^{+2}, suggesting some amount of dry contamination of the monthly wet only samples. Also, since both SO_4^{-2} and NO_3^- correlate well with Ca^{+2} and Mg^{+2}, even with the A sampler, during drier windier sampling days (Table III-15) suggests that some of the extra SO_4^{-2} and NO_3^- in the monthly samples is due to dry contamination. Furthermore, the extent of the dry contamination for NO_3^- may be masked to some degree by the competing process of volatilization of HNO_3, due to the rather high vapour

pressure of HNO_3 over this type of solution [8]. In other words, dry contamination would tend to increase the NO_3^- in the monthly samples whereas the competing process of volitilization would tend to reduce it. The situation is further complicated by the possible participation of microbial consumption of NO_3^- in the monthly samplers. [9, 10]

For Cl^-, the summed event data are greater than the monthly data, suggesting that the chloride in solution in the monthly samplers is lost by volitization or some other mechanism.

For K^+ and Na^+, the observed concentrations are so close to the detection limit of the analytical method as to render futile any attempt in the rationalization of these results.

Although there are only two months of complete data upon which the monthly vs the summed event comparisons can be made, the results obtained do suggest that some caution is required in the use of monthly data, even when obtained with a wet only sampler.

III-E Ion Balance Calculations

If all the major ions have been accounted for, then the sum of the anion equivalents will equal the sum of the cation equivalents. The concentration of each precipitation constituent for each month, in micro-equivalents per litre of solution, is given in Table III-24. The anions and cations are summed by month and ratioed in Table III-25. As can be seen from Table III-25, for October, the ionic balance from

the summed event data is virtually identical to that obtained from the monthly data. For September, the balance calculated from the monthly data is better than that obtained with the summed event data. This apparently "better" ion balance for the monthly sampler could well be misleading as the fact that the concentration equivalents of anion and cations in the monthly sampler is $\simeq$ 50% greater than that obtained with the summed event data, suggesting that dry contamination was very significant in the monthly samples for September. This is certainly consistent with the fact that September was an unusually dry month (Table III-23), thus increasing the possibility of dry contamination.

The observed results for the summed anion and cations is similar to those obtained in other recent studies (11).

III-F Servicing and Maintenance Considerations

Of the three designs tested, the S sampler was the most trouble free and easiest to use. This is not surprising as with this sampler, there is virtually nothing that can malfunction. Initial problems with the sensor and recorder signal mechanisms were encountered with the A sampler and, although troublesome at first, were virtually trouble free for the rest of the study period. The F sampler gave the most trouble of the three types used. The problems encountered were of a practical nature and resulted mainly from a design which made changing the bottle rather awkward. Also, the 1/16" polyethylene was found to become brittle during cold days (T $\leq$ 3 °C), necessitating very careful handling.

Regarding the quantity of rain captured, the S sampler was the best and the A the poorest. However, the A sampler did capture enough rain for subsequent analysis on about 88% of the events.

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SUMMARY OF PREVAILING CONDITIONS

EVENT	DAY 1	Rainfall R (mm)	% time wet	% time dry	$\overline{U}$ (km/hr)		REMARKS
					$\overline{U}_d$ *	$\overline{U}_w$ *	
1	22/8	0.51	5.7	94.0	9.6	13.0	Overcast, humid, very light shower
2	23/8	35.0	34.0	66.0	7.2	14.0	Heavy rain overnight, humid in afternoon
3	28/8	1.5	16.0	84.0	7.2	9.2	Fog in AM of 28/8 and 29/8, winds light, A "flip-flopping".
4	29/8	T	-	-	-	12.0	Fog in AM of 29/8 and 30/8, winds mostly light, A's not closing
5	30/8	0.25	-	-	18.0	12.0	Fog in Am 30/8 and some 31/8, winds mostly light, A2 not operational till 1430, evidence of dew
6	2/9	0.25	5.4	95.0	21.0	12.0	Few light showers, winds light to moderate, A2 not operational evidence of dew, feces in S2
7	6/9	0.51	7.4	93.0	18.0	15.0	Scattered light showers, ground damp, winds light to moderate, humid, bird feces S1, birds in vicinity
8	10/9	2.5	19.0	81.0	12.0	11.0	Sunny early AM, thunder shower near noon, strong winds till noon then light to moderate, no birds
9	13/9	31.0	36.0	64.0	16.0	12.0	Heavy haze/fog, winds light to moderate, A2 not working, birds in vicinity on installation, heavy rain midnight onwards
10	14/9	5.8	10.0	90.0	21.0	15.0	Rain till noon, winds strong till 1800 then light to moderate, S's installed at 1000, A2 open whole period
11	1/10	9.9	17.0	83.0	11.0	6.3	Clear, warm all day 1/10; winds light, rain from 0300 to 0900, 2/15, humid and hazy afterwards
12	2/10	2.8	4.5	96.0	14.0	14.0	Hazy and light winds; overcast 2/10; winds light to moderate, rain 0600 to 0800 3/10
13	3/10	1.8	3.2	97.0	6.2	10.0	Haze-fog then overcast 3/10; winds light to moderate; light rain AM of 4/10; birds in vicinity

SUMMARY OF PREVAILING CONDITIONS

EVENT	DAY 1	Rainfall R(mm)	% time wet	% time dry	$\bar{U}_d$ (km/hr)	$\bar{U}_w$ (km/hr)	REMARKS
14	4/10	17.0	49.0	51.0	11.0	7.9	Light steady rain; winds light to moderate; AM of 5/10 clear and cool; birds in vicinity.
15	6/10	8.1	-	-	18.0	19.0	Overcast with rain in evenings, winds light to moderate; recorder not turned on.
16	8/10	12.0	50.0	50.0	11.0	13.0	Clear and cool in AM of 8/10; then overcast and rain starting late PM; many birds in vicinity on AM of 9/10
17	11/10	6.1	41.0	59.0	15.0	15.0	Clear and cold in AM of 11/10; overcast in PM with thunder-storms and rain till 0700 12/10, many birds AM of 12/10.
18	12/10	2.8	15.0	85.0	12.0	13.0	Overcast with light rain 12/10; clear and cold AM of 13/10; winds light to moderate; no birds AM 13/10.
19	17/10	1.3	11.0	89.0	2.1	5.0	Very fine rain AM 14/10; A's "flip-flopping"; light winds; haze-mist on 18/10; birds AM of 17/10.
20	19/10	1.8	8.4	92.0	14.2	12.0	Heavy fog AM 19/10; scattered showers during day; no birds AM 19/10; to moderate winds; clear AM 20/10.
21	20/10	0.5	5.3	95.0	17.0	16.0	Clear AM 20/10; cloudy PM; light thundershowers mid-PM; clear and warm AM 21/10; birds in vicinity.
22	22/10	1.8	2.5	98.0	16.0	17.0	Clear and warm all of 22/10; winds light to moderate; no birds AM 22/10; rain 0730 -0930 on 23/10.
23	23/10	2.8	11.0	89.0	20.0	12.0	Rain AM 23/10; many birds in vicinity AM 23/10; winds strong AM to moderate PM: cold AM 24/10, very large no.of birds.
24	27/10	3.0	21.0	79.0	20.0	12.0	Clear and cool AM 27/10; rain during evening; no birds; gusty winds on AM 27/10.
25	1/11	5.1	31.0	69.0	16.0	13.0	Rain immediately after sampler installation; clear and cool AM 2/11; winds light to moderate.
26	6/11	3.8	31.0	69.0	9.0	14.0	Occasional rain and drizzle; winds light to moderate 6/11, moderate to strong 7/11; clear from 0200 7/11.
27	8/11	0.5	3.5	97.0	22.0	12.0	Cloudy and cold AM 8/11; strong winds; snow shower PM 8/11; winds light and very cold (0^{o}) AM 9/11.
28	9/11	11.0	38.0	62.0	16.0	12.0	Overcast and cold AM 9/11; light to moderate winds AM 9/11; rain 1400 on 9/11 to midnight; partly cloudy and cool AM 10/11, no birds.

SUMMARY OF PREVAILING CONDITIONS

EVENT	DAY 1	Rainfall R(mm)	% time wet	% time dry	$\bar{U}_d$ (km/hr)	$\bar{U}_w$ (km/hr)	REMARKS
29	15/11	2.0	-	-	2.4	15.0	Snowshowers changed to rain later in day 15/11; winds changed from light to strong; sharp drop in temperature 16/11; cold.
30	21/11	6.9	-	-	9.9	16.0	Overcast with rainshowers in evening; warm with light to moderate; no birds on 21/11.
31	26/11	1.0	1.9	98.0	26.0	31.0	Occasional rain AM 26/11; very strong winds AM 26/11; birds in vicinity; no rain from 1200 onwards but ground very wet.
32	27/11	7.9	24.0	76.0	12.0	16.0	Snow and rain from 2100 27/11 to 0900 28/11; winds variable light to strong; ground damp.

*$\bar{U}d$ = average wind speed during dry periods

$\bar{U}w$ = average wind speed during wet periods

Table III-2

All Events

Variance Within Sampler Types

		NH_4^+	K^+	Na^+	Ca^{+2}	Mg^{+2}	Cl^-	Con	F^-	H^+	NO_3^-	R	SO_4^{-2}
A	S_G	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	T	0.9272	0.6263	1.0627	0.8760	0.3613	0.4805	1.1347	1.5006	1.5333	0.1470	1.4031	1.2497
	N	21	21	23	21	22	21	22	22	23	23	23	22
F	S_G	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	S*	NS
	T	1.3978	1.2278	0.7927	0.1244	0.5842	1.1826	0.1732	0.3538	0.5416	0.0961	2.1376	0.18839
	N	27	26	26	26	28	25	25	26	26	25	28	26
S	S_G	NS	NS	NS	NS	NS	NS	NS	NS	S	NS	NS	NS
	T	0.8244	0.8866	0.1326	0.9113	0.7588	0.2060	0.7009	0.0000	2.5421	0.2865	0.4937	0.8962
	N	27	25	27	26	29	24	28	27	26	28	27	27

S_G S = Significant (S) or Not Significant (NS) at 95 %
T T = Paired T Test Value
N N = Number of Events
R = Rainfall Recovery
*NS at 98 %

Table III-3

All Events

Variance Between Sampler Types

		NH_4^+	K^+	Na^+	Ca^{+2}	Mg^{+2}	Cl^-	Con	F^-	H^+	NO_3^-	R	SO_4^{-2}
A & F	S_G	NS	S	S	S	S	S	NS	S	S	S	NS	S
	T	1.9400	5.5881	4.5800	4.5978	3.9293	2.6476	0.7323	2.7274	3.1308	4.6678	0.8154	5.1074
	N	26	25	26	26	27	24	23	26	26	26	28	26
A & S	S_G	NS	S	NS*	S	S	NS	NS	NS*	S	S	NS	S
	T	1.3670	2.3420	1.7834	3.7970	3.1070	1.0039	0.3524	1.7688	2.2911	3.7534	0.6562	4.0689
	N	26	25	26	25	27	23	23	26	26	26	27	26

S_G S = Significant (S) or Not Significant (NS) at 95 *
T T = Paired T Test Value
N N = Number of Events
R = Rainfall Recovery
* S at 90 %

Table III-4

$$\frac{[H^+] \text{ in Sampler "X"}}{[H^+] \text{ in Aerochem Metrics Sampler}}$$

Event	Fav/Aav	Sav/Aav
1	0.73	0.17
2	1.04	1.06
7	0.097	0.027
8	0.39	0.42
9	0.56	0.87
10	0.34	1.36
11	0.89	0.99
12	0.71	0.60
13	0.69	0.65
14	0.77	0.77
15	1.03	1.66
16	0.75	1.01
17	0.98	0.96
18	0.87	0.89
19	0.29	0.86
20	0.41	0.27
21	0.45	0.24
22	0.23	0.015
23	0.47	1.10
24	1.44	0.93
25	0.97	0.98
26	0.84	0.95
27	3.9	0.46
28	0.47	0.85
29	1.14	0.83
30	0.99	0.92
31	2.3	2.9
32	0.96	1.16
Average Ratio	0.88	0.85
	(0.71) *	(0.78) **

* Ratios for events # 27 & 31 omitted

** Ratios for event # 31 omitted

TABLE III - 5

AEROCHEM METRICS SAMPLER

CORRELATION COEFFICIENT MATRIX

ALL EVENTS

n ≅ 25

	H^+	NO_3^-	SO_4^{-2}	NH_4^+	CL^-	F^-	COND	CA^{+2}	MG^{+2}	NA^+
NO_3^-	.64									
SO_4^{-2}	.67	.71								
NH_4^+	.34	.58	.50							
CL^-	-.05	.35	.26	.04						
F^-	.01	.39	.34	.20	.30					
COND	.93	.86	.92	.84	.16	.23				
CA^{+2}	.01	.33	.56	-.06	.41	.32	.07			
MG^{+2}	-.03	.25	.47	-.07	.44	.31	.01	.94		
NA^+	-.15	.19	.37	-.21	.64	.18	-.03	.56	.47	
K^+	-.12	.21	.40	.44	.23	.25	.40	.45	.22	.32

TABLE III - 6

FUNNEL AND BOTTLE SAMPLER

CORRELATION COEFFICIENT MATRIX

ALL EVENTS

$n \cong 25$

	H^+	NO_3^-	SO_4^{-2}	NH_4^+	Cl^-	F^-	Cond	Ca^{+2}	Mg^{+2}	Na^+
NO_3^-	.45									
SO_4^{-2}	.42	.80								
NH_4^+	.33	.74	.62							
Cl^-	-.09	.64	.53	.35						
F^-	.20	.52	.39	.30	.51					
Cond	.77	.82	.76	.67	.44	.26				
Ca^{+2}	-.21	.53	.60	.27	.77	.57	.32			
Mg^{+2}	-.11	.45	.64	.34	.59	.40	.36	.80		
Na^+	-.34	-.04	.04	-.05	.26	.30	-.20	.44	.47	
K^+	-.06	.66	.51	.71	.63	.65	.45	.62	.57	.32

TABLE III - 7

SUDBURY EVENT SAMPLER

CORRELATION COEFFICIENT MATRIX

ALL EVENTS

N ≅ 25

NO_3^-	.31									
SO_4^{-2}	.09	.70								
NH_4^+	.12	.46	.48							
Cl^-	-.11	.55	.58	.05						
F^-	-.01	.62	.56	.10	.52					
Cond	.73	.78	.76	.34	.38	.41				
Ca^{+2}	-.32	.34	.69	.25	.30	.56	.18			
Mg^{+2}	-.30	.54	.58	.17	.80	.48	.33	.72		
Na^+	-.40	.39	.69	.42	.69	.35	.14	.53	.61	
K^+	-.32	.35	.62	.44	.40	.31	.16	.48	.44	.82
	H^+	NO_3^-	SO_4^{-2}	NH_4^+	Cl^-	F^-	Cond	Ca^{+2}	Mg^{+2}	Na^+

Table III - 8

<u>AEROCHEM METRICS SAMPLER</u>

R ≥2.8 MM

n ≅ 15

	H^+	NO_3^-	SO_4^{-2}	NH_4^+	Cl^-	F^-	Cond	Ca^{+2}	Mg^{+2}	Na^+	K^+
NO_3^-	.74										
SO_4^{-2}	.89	.77									
NH_4^+	.80	.89	.88								
Cl^-	.16	.19	-.03	.18							
F^-	.21	.51	.26	.28	-.12						
Cond	.95	.88	.97	.89	.15	.36					
Ca^{+2}	.18	.57	.30	.28	-.11	.49	.42				
Mg^{+2}	-.04	.31	.01	.01	.33	.33	.14	.67			
Na^+	-.36	-.24	-.13	-.28	-.15	-.18	-.17	.01	.12		
K^+	.42	.45	.47	.50	-.31	.22	.48	.13	-.51	-.36	
Vol	.23	-.31	.14	-.05	-.06	-.42	-.03	-.22	-.44	-.24	.48

Table III - 9

FUNNEL AND BOTTLE SAMPLER

$R \geq 2.8$ MM

$n \cong 15$

NO_3^-	.81										
SO_4^{-2}	.89	.79									
NH_4^+	.81	.89	.87								
Cl^-	.37	.57	.30	.35							
F^-	.42	.51	.36	.30	.31						
COND	.95	.88	.86	.82	.48	.49					
Ca^{+2}	.18	.41	.27	.16	.25	.64	.29				
Mg^{+2}	.34	.47	.56	.44	.10	.39	.35	.80			
Na^+	-.42	-.48	-.37	-.51	-.32	-.09	-.49	-.09	-.05		
K^+	.28	.48	.27	.35	.13	.78	.43	.52	.35	.21	
VOL	.07	-.37	-.03	-.25	-.38	-.38	-.05	-.21	-.06	-.04	-.51
	H^+	NO_3^-	SO_4^{-2}	NH_4^+	Cl^-	F^-	COND	Ca^{+2}	Mg^{+2}	Na^+	K^+

Table III - 10

SUDBURY EVENT SAMPLER

$R \geq 2.8$ MM

$n \cong 15$

NO_3^-	.71										
SO_4^{-2}	.96	.72									
NH_4^+	.36	.44	.33								
Cl^-	.25	.20	.25	-.05							
F^-	.28	.46	.38	.04	.07						
Cond	.96	.78	.97	.32	.29	.41					
Ca^{+2}	.02	-.03	.12	.03	-.38	.31	.09				
Mg^{+2}	.62	.71	.77	.32	.45	.58	.75	.15			
Na^+	-.18	-.12	-.04	-.10	.31	.01	-.08	-.23	.17		
K^+	.35	.28	.37	.32	-.33	.20	.29	-.21	.24	-.26	
Vol	.15	-.36	.03	-.27	.51	-.36	.02	-.32	-.32	-.23	.07
	H^+	NO_3^-	SO_4^{-2}	NH^+	Cl^-	F^-	Cond	Ca^{+2}	Mg^{+2}	Na^+	K^+

Table III - 11.

AEROCHEM METRICS SAMPLER

$\overline{U}$. f $\leq$ 11 km/hr

n $\cong$ 12

	H^+	NO_3^-	SO_4^{-2}	NH_4^+	CL^-	F^-	COND	CA^{+2}	MG^{+2}	NA^+	K^+
NO_3^-	.75										
SO_4^{-2}	.96	.76									
NH_4^+	.82	.90	.84								
CL^-	-.01	.20	-.12	.21							
F^-	.22	.53	.21	.23	-.03						
COND	.97	.89	.97	.88	.12	.39					
CA^{+2}	.35	.00	.37	.11	-.25	-.11	-.08				
MG^{+2}	-.16	-.04	-.12	-.02	-.07	-.15	-.16	.97			
NA^+	-.17	-.03	-.06	-.18	.04	-.15	.01	-.10	-.05		
K^+	.56	.42	.49	.51	-.38	.17	.54	-.07	-.59	-.41	
VOL	.13	-.53	.07	-.27	-.24	-.39	-.17	-.34	-.40	-.17	.36

Table III - 12

FUNNEL AND BOTTLE SAMPLER

$\bar{U}$. f $\leq$ 11 km/hr

n $\cong$ 12

	H^+	NO_3^-	SO_4^{-2}	NH_4^+	Cl^-	F^-	Cond	Ca^{+2}	Mg^{+2}	Na^+	K^+
NO_3^-	.60										
SO_4^{-2}	.80	.76									
NH_4^+	.59	.90	.86								
Cl^-	-.09	.50	.08	.42							
F^-	.49	.55	.27	.31	.31						
Cond	.88	.81	.80	.75	.28	.30					
Ca^{+2}	-.25	.29	.15	.20	.10	.13	.44				
Mg^{+2}	.13	.50	.50	.50	.25	.07	.67	.82			
Na^+	-.41	-.59	-.54	-.67	-.14	-.16	-.57	-.14	-.15		
K^+	.23	.65	.25	.44	.78	.76	.57	.29	.29	-.32	
Vol	.07	-.67	-.24	-.54	-.66	-.39	-.38	-.56	-.46	.22	-.62

Table III - 13

SUDBURY EVENT SAMPLER

$\bar{U}$. f $\leq$ 11 km/hr

n $\cong$ 12

NO_3^-	.67										
SO_4^{-2}	.81	.73									
NH_4^+	.64	.87	.85								
Cl^-	.10	.34	.00	.17							
F^-	.28	.61	.29	.38	.27						
Cond	.95	.84	.92	.79	.14	.41					
Ca^{+2}	-.11	.36	.45	.51	-.15	.23	.12				
Mg^{+2}	.16	.70	.58	.78	.43	.45	.30	.81			
Na^+	-.07	.32	.08	.22	.73	.30	.08	.22	.60		
K^+	.15	.44	.31	.52	.45	.40	.25	.34	.67	.45	
Vol	.09	-.58	-.25	-.53	-.03	-.51	-.16	-.65	-.73	-.49	-.29
	H^+	NO_3^-	SO_4^{-2}	NH_4^+	Cl^-	F^-	Cond	Ca^{+2}	Mg^{+2}	Na^+	K^+

Table III - 14

AEROCHEM METRICS SAMPLER

R < 2.8 MM

n ≅ 9

	H^+	NO_3^-	SO_4^{-2}	NH_4^+	Cl^-	F^-	Cond	Ca^{+2}	Mg^{+2}	Na^+	Vol
NO_3^-	.74										
SO_4^{-2}	.60	.50									
NH_4^+	-.27	.05	-.30								
Cl^-	.40	.50	.59	-.59							
F^-	-.04	.08	.23	-.14	.56						
Cond	.98	.88	.63	.81	.38	-.14					
Ca^{+2}	.48	.25	.93	-.51	.19	.15	-.30				
Mg^{+2}	.57	.15	.80	-.51	.08	.18	-.24	.91			
Na^+	.25	.26	.60	-.62	.75	.07	.23	.36	.18		
K^+	-.24	.05	.36	.40	.01	.04	-.03	.25	-.11	.09	
Vol	-.01	-.25	-.36	-.02	-.70	-.58	-.21	.15	.36	-.50	-.73

Table III - 15

AEROCHEM METRICS SAMPLER

$\overline{U}$. f > 11 km/hr

n $\cong$ 10

NO_3^-	.45										
SO_4^{-2}	.28	.64									
NH_4^+	-.37	.04	.08								
Cl^-	.08	.63	.70	-.09							
F^-	-.17	.13	.50	.10	.58						
Cond	.77	.81	.70	.76	.42	-.06					
Ca^{+2}	.28	.71	.92	-.18	.76	.59	.58				
Mg^{+2}	.34	.61	.86	-.18	.80	.72	.58	.92			
Na^+	.08	.50	.68	-.25	.79	.18	.40	.68	.62		
K^+	-.31	.34	.48	.63	.30	.30	-.24	.38	.13	.22	
Vol	.00	-.26	-.62	-.23	-.62	-.41	-.46	-.48	-.50	-.52	-.42
	H^+	NO_3^-	SO_4^{-2}	NH_4^+	Cl^-	F^-	Cond	Ca^{+2}	Mg^{+2}	Na^+	K^+

Table III - 16

FUNNEL AND BOTTLE SAMPLER

$R < 2.8$ MM

$n \cong 9$

NO_3^-	.50										
SO_4^{-2}	.25	.65									
NH_4^+	-.12	.46	.13								
Cl^-	.43	.67	.41	.10							
F^-	.07	.40	.23	.16	.72						
COND	.34	.80	.60	.50	.83	-.10					
Ca^{+2}	.03	.50	.66	.03	.66	.71	.16				
Mg^{+2}	.08	.29	.65	.12	.41	.39	.24	.65			
Na^+	.25	.42	.44	.28	.55	.80	.47	.71	.75		
K^+	.24	.87	.54	.86	.59	.59	.78	.44	.42	.62	
VOL	-.34	-.39	-.45	-.06	-.65	-.39	-.13	-.39	-.07	-.10	-.44
	H^+	NO_3^-	SO_4^{-2}	NH_4^+	Cl^-	F^-	COND	Ca^{+2}	Mg^{+2}	Na^+	K^+

Table III - 17

SUDBURY EVENT SAMPLER

R < 2.8 MM

n ≅ 10

NO_3^-	.21										
SO_4^{-2}	-.37	.63									
NH_4^+	-.22	.40	.66								
Cl^-	.31	.84	.54	.11							
F^-	.17	.72	.50	-.05	.63						
Cond	.19	.93	.67	.42	.83	.55					
Ca^{+2}	-.45	.57	.91	.37	.42	.60	.53				
Mg^{+2}	-.25	.59	.37	.02	.78	.37	.66	.79			
Na^+	-.26	.46	.71	.84	.56	.19	.42	.47	.35		
K^+	-.28	.37	.54	.69	.18	.27	.34	.48	.12	.76	
Vol	-.23	-.36	-.43	-.34	-.55	-.40	-.45	-.46	-.33	-.61	-.60
	H^+	NO_3^-	SO_4^{-2}	NH_4^+	Cl^-	F^-	Cond	Ca^{+2}	Mg^{+2}	Na^+	K^+

Table III - 18

FUNNEL AND BOTTLE SAMPLER

$\overline{U}$. f $\geq$ 11 km/hr

n $\cong$ 10

NO_3^-	.32										
SO_4^{-2}	.02	.83									
NH_4^+	-.08	.59	.46								
Cl^-	.10	.79	.76	.35							
F^-	-.15	.51	.48	.33	.65						
COND	.41	.89	.80	.61	.79	.53					
Ca^{+2}	-.09	.74	.79	.35	.92	.80	.75				
Mg^{+2}	-.14	.54	.75	.38	.64	.55	.56	.77			
Na^+	-.25	.14	.19	.15	.28	.49	.09	.43	.48		
K^+	-.21	.83	.67	.91	.55	.62	.65	.64	.58	.37	
VOL	.10	-.51	-.69	-.40	-.53	-.41	-.60	-.58	-.45	.01	-.53
	H^+	NO_3^-	SO_4^{-2}	NH_4^+	Cl^-	F^-	COND	Ca^{+2}	Mg^{+2}	Na^+	K^+

Table III - 19

SUDBURY EVENT SAMPLER

$\overline{U}$. f $\geq$ 11 km/hr

n $\cong$ 10

	H^+	NO_3^-	SO_4^{-2}	NH_4^+	Cl^-	F^-	Cond	Ca^{+2}	Mg^{+2}	Na^+	K^+
NO_3^-	-.29										
SO_4^{-2}	-.57	.72									
NH_4^+	.16	.36	.36								
Cl^-	-.48	.70	.83	-.02							
F^-	-.31	.65	.69	-.05	.63						
Cond	-.34	.78	.85	.30	.80	.63					
Ca^{+2}	-.39	.44	.77	.11	.46	.75	.67				
Mg^{+2}	-.52	.66	.59	.04	.91	.53	.79	.68			
Na^+	-.62	.56	.84	.40	.77	.36	.64	.50	.57		
K^+	-.63	.42	.68	.34	.40	.43	.43	.37	.33	.84	
Vol	.14	-.32	-.64	-.28	-.46	-.42	-.52	-.56	-.52	-.57	-.55

TABLE III-20

Rainfall Recovery Ratios

	V_A (ml)	VSo (ml)	R_A (mm)	RSo (mm)	RTB (mm)	R_A/RTB
August	2361*	2375	41*	77.9	37.6*	1.09*
September	2795	1310	43.5	43	40.1	1.08
October	5139	2425	80	79.5	72.6	1.10
November	2711*	2320	42.2*	76.1	38.2	1.10*

* Partial Month Only

V_A = Total volume of rainfall collected by the Aerochem Metrics 2 (A) sampler.

R = Rainfall amount measured with the A and SO samplers, and with the Tipping Bucket (TB) gauge.

So sampler collection area = 305 cm^2

A sampler collection area = 642 cm^2

Table III - 21

Data From MOE/ARB Monthly Wet Only Sampler ("Sangamo")

Parameter	August/79	September/79	October/79	November/79
pH	3.92	4.37	3.90	4.16
H^+ (M)	1.20×10^{-4}	4.27×10^{-5}	1.26×10^{-4}	$6.29 \times 10^{-}$[illegible]
$SO_4^=$ (mg/l)	6.35	3.35	6.50	3.65
$N\text{-}NO_3^-$ (mg/l)	0.77	0.32	1.23	0.79
$N\text{-}NH_4^-$ (mg/l)	0.26	0.16	0.83	0.33
Ca^{++} (mg/l)	0.39	0.56	0.71	0.52
Na^+ (mg/l)	0.02	0.02	0.04	0.09
K^+ (mg/l	0.03	0.02	0.06	0.02
Mg^{++} (mg/l)	0.08	0.14	0.13	0.10
Cl^- (mg/l)	0.25	0.13	0.33	0.37
Volume (ml)	2375	1310	2425	2320
Storage G. (mm)	n/a	n/a	n/a	80
Collection Dates	July 31 - Aug. 31	Aug 31 - Sept. 28	Sept. 28 - Nov. 1	Nov. 1 - Nov. 30

$A_A \sim 642\ cm^2$ $\quad r_A \sim 14.3$ cm

$A_{So} \sim 305\ cm^2$ $\quad r_{So} \sim 9.9$ cm

Table III-22

Comparison of Monthly Wet Only ("Sangamo")
with
Summed Event Data ("Aerochem Metrics")

	H^+			SO_4^{-2}			NO_3^{-1}			NH_4^{+1}		
	M	ΣE	ΣE/M	M	ΣE	ΣE/M	M	ΣE	ΣE/M	M	ΣE	ΣE/M
AUG.	1.20(-4)	1.49(-4) *		6.35	6.03*		3.41	2.49*		0.34	0.393*	
SEPT.	4.27(-5)	2.57(-5)	0.60	3.35	1.60	0.48	1.42	0.945	.68	0.21	0.131	.64
OCT.	1.26(-4)	1.18(-4)	0.94	6.50	5.33	0.82	5.45	4.88	.90	1.07	0.945	.85
NOV.	6.92(-5)	4.84(-5) *		3.65	2.44*		3.50	3.27*		0.43	0.301*	

	Ca^{+2}			Mg^{+2}			Cl^{-1}			K^{+}**			Na^{+}**		
	M	ΣE	ΣE/M	M	ΣE	ΣE/M	M	ΣE	ΣE/M	M	ΣE	ΣE/M	M	ΣE	ΣE/M
AUG.	0.39	0.51		0.08	0.149*		0.25	0.08*		0.03	0.315*		0.02	0.087*	
SEPT.	0.56	0.46	0.82	0.14	0.045	0.32	0.13	0.15	1.2	0.02	0.042		0.02	0.052	
OCT.	0.71	0.49	0.69	0.13	0.053	0.41	0.33	0.79	2.4	0.06	0.072		0.04	0.049	
NOV.	0.52	0.41*		0.10	0.055*		0.37	0.55 *		0.02	0.037 *		0.09	0.121 *	

Concentration in mg/litre except for H^+ which is given in moles/litre

M = Monthly Wet Only (Sangamo)

ΣE = Summed Event Data (Aerochem Metrics)

* = Partial Month Only

** = Values near or at detection limit, thus ratios not meaningful

Table III-23

Rainfall Amount (R) in mm

	Aug.	Sept.	Oct.	Nov.	Σ (Sept.,Oct.)
+Mean 1941-70	69.3	61.2	58.4	61.0	120
This Study 1979	37.6*	40.1	72.6	38.2*	112.7

+ From reference #7

* Partial month only

Table III - 24

Precipitation Composition in $\mu eq/l$

	H^+		SO_4^{-2}		NO_3^-		NH_4^+		Ca^{+2}		Mg^{+2}		Cl^-		K^+		Na^+		F^-	
	M	ΣE	M	ΣE	M	ΣE	M	ΣE	M	ΣE	M	ΣE	M	ΣE	M	ΣE	M	ΣE	M	ΣE
August	120.0	149.0*	132.0	126.0*	54.9	40.2*	18.6	21.8*	19.5	25.4*	6.58	12.2*	7.05	2.26*	.767	8.06*	.870	3.78*	-	2.7*
September	42.7	25.7	69.8	33.3	22.9	15.2	11.4	7.26	27.9	23.0	11.5	3.70	3.67	4.23	.512	1.07	.870	2.26	-	0.37
October	126.0	118.0	135.0	111.0	87.7	78.7	59.3	52.4	35.4	24.4	10.7	4.35	9.31	22.3	1.53	1.84	1.74	2.13	-	4.4
November	69.2	48.4*	76.0	50.8*	56.3	45.8*	23.6	16.7*	26.0	20.5*	8.22	4.52*	10.4	15.5*	.512	.946*	3.91	5.26*	-	3.6*

M = Monthly Wet Only (Sangamo)
Σ = Summed Event Data (Aerochem Metrics)
* = Partial Month Only

Table III - 25

Summation of Anions and Cations

		Σ Cations (μeq/l)	Σ Anions (μeq/l)	Σ Anions / Σ Cations
August	M	166	195	1.13
	ΣE	220.3	168.0 (171.)*	0.76 (0.78)* } †
September	M	94.9	96.3	1.01
	ΣE	62.9	52.8 (53.2)*	0.84 (0.85)*
October	M	235	232	0.99
	ΣE	203.2	212.0 (216.0)*	1.04 (1.06)*
November	M	131	143	1.09
	ΣE	196.3	112.1 (116.0)*	1.16 (1.20)* } †

† = partial month's data only
* = F^- included in calculations

Appendix A

Parameter Concentration Matrices

Legend

a.= sampler malfunction

b = insufficient sample

c = below detection limit

d = beyond calibration range

e = off scale

f.= data missing

H_3O^+ = number in column x $10^{\text{number in brackets}}$

EVENT #	A1	A2	A av.	F1	F2	F av.	S1	S2	S av.	COMMENTS
1	4.17(-6)	1.95(-4)	0.996(-4)	7.24(-5)	7.41(-5)	7.32(-5)	2.19(-5)	1.26(-5)	1.72(-5)	Contamination suspected measured 24 hr after retreived.
2	1.51(-4)	1.48(-4)	1.49(-4)	1.48(-4)	1.62(-4)	1.55(-4)	1.66(-4)	1.51(-4)	1.58(-4)	
4	—	—	—	—	—	—	1.66(-6)	2.40(-6)	2.03(-6)	
5	—	—	—	—	—	—	3.47(-8)	3.24(-8)	3.35(-8)	
6	—	—	—	—	—	—	3.63(-4)	1.86(-4)	2.74(-4)	
7	5.89(-5)	2.75(-5)	4.32(-5)	4.90(-6)	3.47(-6)	4.18(-6)	1.20(-6)	1.12(-6)	1.16(-6)	A2 left open for 24 hrs.
8	1.07(-5)	—	—	5.13(-6)	3.31(-6)	4.22(-6)	4.79(-6)	4.27(-6)	4.53(-6)	
9	2.82(-5)	—	—	2.14(-5)	9.77(-6)	1.57(-5)	2.57(-5)	2.34(-5)	2.45(-5)	
10	2.19(-5)	—	—	1.35(-5)	1.70(-6)	0.76(-5)	2.95(-5)	3.02(-5)	2.98(-5)	Contamination suspected
11	2.87(-4)	3.09(-4)	2.95(-4)	2.63(-4)	2.63(-4)	2.63(-4)	3.02(-4)	2.82(-4)	2.92(-4)	
12	1.91(-4)	1.29(-4)	1.60(-4)	1.00(-4)	1.29(-4)	1.14(-4)	1.02(-4)	8.91(-5)	0.955(-4)	
13	1.45(-4)	1.00(-4)	1.22(-4)	7.41(-5)	9.33(-5)	8.37(-5)	8.71(-5)	7.24(-5)	7.97(-5)	
14	1.29(-4)	1.26(-4)	1.27(-4)	1.05(-4)	9.12(-5)	0.981(-4)	1.10(-4)	8.51(-5)	0.975(-4)	
15	5.37(-5)	5.37(-5)	5.37(-5)	5.89(-5)	5.13(-5)	5.51(-5)	1.15(-4)	6.31(-5)	0.890(-4)	
16	4.57(-5)	4.57(-5)	4.57(-5)	2.88(-5)	3.98(-5)	3.43(-5)	4.57(-5)	4.68(-5)	4.62(-5)	
17	1.00(-4)	9.12(-5)	0.956(-4)	9.33(-5)	9.33(-5)	9.33(-5)	9.33(-5)	9.12(-5)	9.22(-5)	
18	2.40(-5)	2.95(-5)	2.67(-5)	2.24(-5)	2.40(-5)	2.32(-5)	2.45(-5)	2.29(-5)	2.37(-5)	
19	1.26(-4)	1.07(-4)	1.16(-4)	1.95(-5)	4.90(-5)	3.42(-5)	1.00(-4)	9.77(-5)	0.998(-4)	
20	1.12(-4)	9.77(-5)	1.05(-4)	6.61(-5)	1.91(-5)	4.26(-5)	2.95(-5)	2.75(-5)	2.85(-5)	
21	8.91(-5)	9.12(-5)	9.01(-5)	1.74(-5)	6.46(-5)	4.10(-5)	1.38(-5)	2.88(-5)	2.13(-5)	
22	6.17(-5)	5.75(-5)	5.96(-5)	1.62(-5)	1.10(-5)	1.38(-5)	9.55(-7)	8.91(-7)	9.23(-7)	
23	4.90(-5)	5.37(-5)	5.13(-5)	3.47(-5)	1.32(-5)	2.39(-5)	5.89(-5)	5.37(-5)	5.63(-5)	
24	1.26(-4)	1.26(-4)	1.26(-4)	1.74(-4)	1.91(-4)	1.82(-4)	1.17(-4)	1.17(-4)	1.17(-4)	
25	6.92(-5)	7.08(-5)	7.00(-5)	7.08(-5)	6.46(-5)	6.77(-5)	6.92(-5)	6.76(-5)	6.84(-5)	
26	1.10(-4)	9.12(-5)	1.01(-4)	7.94(-5)	9.12(-5)	8.53(-5)	9.77(-5)	9.33(-5)	9.55(-5)	
27	5.25(-6)	9.77(-6)	7.51(-6)	2.94(-5)	2.88(-5)	2.91(-5)	4.68(-6)	2.24(-6)	3.45(-6)	
28	2.95(-5)	3.89(-5)	3.42(-5)	2.04(-5)	1.17(-5)	1.60(-5)	3.02(-5)	2.82(-5)	2.92(-5)	
29	2.75(-5)	5.01(-5)	3.88(-5)	3.81(-5)	5.01(-5)	4.41(-5)	4.17(-5)	2.29(-5)	3.23(-5)	
30	2.45(-5)	3.31(-5)	2.88(-5)	2.82(-5)	2.88(-5)	2.85(-5)	2.51(-5)	2.82(-5)	2.66(-5)	
31	1.41(-6)	2.00(-5)	1.07(-5)	2.14(-5)	2.75(-5)	2.44(-5)	2.24(-5)	3.98(-5)	3.11(-5)	
32	6.03(-5)	5.75(-5)	5.89(-5)	5.89(-5)	5.37(-5)	5.63(-5)	6.76(-5)	6.92(-5)	6.84(-5)	

Sulfate ± 0.05 mg/l Calibrated Range = 0.00-15.00 mg/l

EVENT #	A1	A2	A av.	F1	F2	F av.	S1	S2	S av.	COMMENTS
1	10.9	10.0	10.4	11.9	11.7	11.8	13.1	13.8	13.5	
2	5.99	5.99	5.99	6.34	6.12	6.24	6.14	6.24	6.19	
4	b	b	b	b	b	b	16.1	20.2	18.1	
5	b	b	b	b	b	b	b	b	b	
6	b	b	b	b	b	b	b	b	b	
7	5.30	a	5.3	5.66	5.47	9.95	7.83	5.24	6.53	
8	6.88	a	6.88	6.73	13.2	6.73	6.93	7.18	7.05	
9	1.19	a	1.19	1.39	1.54	1.46	1.34	1.39	1.36	
10	0.94	a	0.94	1.13	1.09	1.11	1.23	1.43	1.33	
11	14.8	15.0	14.9	15.3	4.08	15.3	15.4	15.7	13.5	
12	3.30	3.06	3.18	4.48	4.11	4.29	4.00	4.16	4.08	
13	b	b	b	b	b	b	b	b	b	
14	3.93	3.90	3.91	4.52	4.41	4.46	4.24	4.27	4.25	
15	3.20	3.26	3.23	3.52	3.85	3.68	2.56	3.68	3.12	
16	1.69	1.63	1.64	1.93	1.58	1.75	1.55	1.14	1.34	
17	5.46	4.94	5.20	5.41	5.48	5.44	5.62	5.85	5.73	
18	f	f	f	1.56	1.56	1.56	1.50	1.72	1.61	
19	4.81	4.13	4.47	5.68	5.20	5.44	6.43	5.95	6.19	
20	7.11	7.26	7.18	9.17	10.0	11.5	9.80	9.72	9.76	
21	8.49	8.66	8.57	14.2	8.71	8.71	9.38	10.8	10.1	
22	6.90	6.86	6.88	9.87	8.68	9.27	9.74	10.3	10.0	F1,F2,S1,S2 contaminate
23	4.05	3.92	3.98	5.13	5.60	5.36	4.14	3.49	3.81	
24	5.17	5.22	5.19	6.51	6.88	6.67	6.14	6.12	6.13	
25	3.87	3.94	3.90	5.54	4.89	5.21	4.76	4.89	4.82	
26	3.12	3.59	3.35	4.52	4.37	4.44	4.24	4.22	4.21	
27	5.69	4.59	5.14	9.98	8.63	9.30	9.01	9.14	9.07	
28	2.19	2.19	2.19	2.79	2.81	2.80	2.35	2.33	2.34	
29	4.29	4.35	4.32	4.02	4.49	4.25	3.70		3.70	
30	1.67	1.83	1.75	2.47	2.55	2.51	2.51	2.38	2.44	
31	2.62	2.60	2.61	2.85	2.70	2.77	3.13	2.79	2.96	
32	1.76	1.73	1.74	2.30	2.19	2.24	2.30	2.25	2.27	

Nitrate ± 0.04 mg/l   Calibrated Range 0.00-10.00 mg/l

EVENT #	A1	A2	A av.	F1	F2	F av.	S1	S2	S av.	COMMENTS
1	7.95	7.71	7.83	11.4	10.2	10.8	10.07	10.4	10.2	
2	2.43	2.45	2.44	2.69	2.52	2.61	2.64	2.69	2.665	
4	___b	___b	___b	___b	___b	___b	7.80	9.54	8.67	
5	___b	___b	___b	___b	___b	___b	___b	___b	___b	
6	___b	___b	___b	___b	___b	___b	___b	___b	___b	
7	3.22	5.89	4.55	4.82	4.77	4.80	5.52	4.69	5.11	
8	3.42	___a	3.42	3.83	7.26	5.55	3.54	3.63	3.59	
9	0.81	___a	0.81	0.93	0.93	0.93	0.89	0.89	0.89	
10	0.35	___a	0.35	0.32	0.35	0.335	0.43	0.59	0.51	
11	10.7	10.8	10.8	11.4	___	11.4	11.21	11.4	11.3	
12	4.33	3.93	4.13	5.46	5.12	5.29	5.83	5.61	5.72	
13	___b	___b	___b	___b	___b	___b	___b	___b	___b	
14	2.93	2.93	2.93	3.36	3.22	3.29	3.22	3.25	3.24	
15	3.81	3.57	5.76	___e	3.94	3.94	5.35	6.79	6.07	F1 contaminated
16	2.24	2.24	2.24	2.41	2.24	2.33	2.03	1.09	1.56	
17	6.36	5.53	5.95	6.36	7.03	6.70	7.13	7.13	7.13	
18	___f	___f	___f	2.70	2.69	2.70	2.47	2.55	6.08	
19	8.15	7.15	7.65	8.87	8.20	8.54	10.03	9.97	10.0	
20	5.36	5.36	5.36	7.31	7.35	7.33	7.06	6.94	7.0	
21	4.13	4.21	4.17	7.79	5.18	6.49	5.23	4.50	4.87	
22	4.65	4.85	4.75	8.96	7.39	8.18	9.60	10.4	9.99	Black particulates in F1,F2,S1,S2
23	1.72	1.49	1.61	3.12	3.44	3.28	1.66	2.29	1.9	
24	6.29	6.16	6.23	8.40	8.62	8.51	7.43	7.43	7.43	
25	2.93	3.04	2.99	4.14	3.72	3.93	3.41	3.55	3.48	
26	6.29	6.27	6.28	8.32	8.07	8.20	8.30	8.47	8.39	
27	4.13	3.43	3.78	10.5	8.78	9.64	6.50	6.44	6.47	
28	1.98	2.04	2.01	2.45	2.52	2.49	2.11	2.16	2.1	
29	5.78	5.91	5.85	5.58	5.54	5.56	4.68	3.34	4.01	
30	1.34	1.49	1.42	2.07	2.19	2.13	1.84	1.77	1.81	
31	1.00	0.98	0.99	1.35	1.30	1.33	1.67	1.11	1.39	
32	3.79	3.62	3.71	5.05	5.00	5.03	4.74	4.71	4.73	

Ammonium mg/l ± .03 mg/l   Calibrated Range 0.00-2.00 mg/l

EVENT #	A1	A2	A av.	F1	F2	F av.	S1	S2	S av.	COMMENTS
1	0.20	0.25	0.225	0.24	0.35	0.295	0.67	0.73	0.700	
2	0.41	0.38	0.395	0.38	0.37	0.375	0.29	0.32	0.305	
4	b	b	b	b	b	b	3.56	4.56	4.06	
5	b	b	b	b	b	b	b	b	b	
6	b	b	b	b	b	b	b	b	b	
7	0.67	a	0.67	0.57	0.53	0.550	0.68	e	e	FS contaminated
8	1.27	a	1.27	1.13	0.99	1.06	1.09	1.13	1.11	
9	0.04	a	0.04	0.03	< 0.01	0.02	0.04	0.02	0.03	
10	<0.01	a	<0.01	<0.01	< 0.01	0.01	<0.01	<0.01	0.01	
11		2.22	2.22	2.24	2.28	2.26	2.16	2.11	2.13	
12	0.43	0.38	0.405	0.57	0.65	0.61	0.59	0.58	0.585	
13	b	b	b	b	b	b	b	b	b	
14	0.87	0.89	0.88	0.89	0.83	0.86	0.83	0.78	0.805	
15	0.75	0.65	0.70	0.48	0.45	0.465	0.97	0.45	0.71	
16	0.31	0.25	0.28	0.29	0.35	0.320	0.29	0.31	0.30	
17	1.32	1.37	1.34	1.28	1.30	1.29	1.26	1.27	1.26	
18	f	f	f	0.75	0.66	0.705	0.62	0.61	0.615	
19	1.22	1.35	1.28	1.41	1.53	1.47	1.71	1.54	1.62	
20	1.13	1.16	1.14	1.41	1.29	1.35	1.32	1.40	1.36	
21	0.64	0.54	0.59	0.96	0.63	0.795	0.66	0.85	0.745	
22	0.82	0.86	0.840	1.30	0.96	1.17	1.31	1.17	1.24	
23	0.46	0.34	0.400	0.53	0.44	0.485	0.27	0.31	0.290	
24	0.77	0.69	0.730	0.97	1.01	0.990	0.87	0.85	0.860	
25	0.42	0.41	0.415	0.64	0.54	0.600	0.45	0.46	0.455	
26	0.65	0.78	0.715	0.84	0.78	0.810	0.72	0.71	0.715	
27	2.60	2.19	2.39	2.95	2.82	2.88	2.39	2.52	2.45	
28	0.13	0.11	0.12	0.21	0.31	0.260	0.21	0.24	0.225	
29	1.24	1.32	1.28	0.96	1.09	1.02	1.13	0.84	0.985	
30	0.03	0.05	0.040	0.11	0.15	0.130	0.08	0.09	0.085	
31	0.30	0.28	0.290	0.28	0.28	0.280	0.25	0.18	0.215	
32	0.38	0.35	0.365	0.51	0.53	0.520	0.45	0.42	0.435	

Chloride ± 0.02 mg/l   Calibrated Range 0.00-2.00 mg/l

EVENT #	A1	A2	A av.	F1	F2	F av.	S1	S2	S av.	COMMENTS
1	1.80	1.68	1.74	1.68	2.32	2.00	1.28	1.64	1.46	
2	0.11	0.01	0.06	0.11	0.05	0.080	—	—	—	
4	— [b]	— [b]	— [b]	— [b]	— [b]	— [b]	— [e]	2.32	—	
5	— [b]	— [b]	— [b]	— [b]	— [b]	— [b]	— [b]	— [b]	— [b]	
6	— [b]	— [b]	— [b]	— [b]	— [b]	— [b]	— [b]	— [b]	— [b]	
7	1.23	1.77	1.50	0.69	0.88	0.785	1.38	0.35	0.865	
8	0.24	— [a]	0.24	0.20	0.51	0.355	0.26	0.23	0.245	
9	0.13	— [a]	0.13	<0.01	0.14	0.073	0.06	0.02	1.04	
10	0.12	— [a]	0.12	0.19	0.08	0.135	0.31	0.26	0.285	
11	0.38	0.69	0.535	1.00	0.20	0.600	0.63	0.66	0.645	
12	0.66	0.59	0.625	0.84	0.34	0.590	0.40	0.24	0.370	
13	— [b]	— [b]	— [b]	— [b]	— [b]	— [b]	— [b]	— [b]	— [b]	
14	14.8	1.77	1.62	<0.01	<0.01	—	<0.01	0.30	—	
15	0.41	0.46	0.435	1.24	0.44	0.840	0.52	0.57	0.545	
16	0.36	0.32	0.340	0.54	0.38	0.460	0.30	0.11	0.205	
17	0.41	0.42	0.415	0.49	0.48	0.485	0.57	0.55	0.560	
18	— [f]	— [f]	— [f]	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
19	1.19	1.23	1.21	2.66	1.50	2.08	1.70	1.62	1.66	
20	0.56	0.96	0.76	1.22	1.38	1.30	1.10	1.11	1.10	
21	— [e]	— [e]	— [e]	2.72	1.50	2.11	1.13	1.58	1.35	
22	2.04	1.44	1.74	2.55	2.17	2.36	2.12	2.13	2.12	
23	< 0.01	<0.01	< 0.01	<0.01	0.34	<0.01	<0.01	<0.01	<0.01	omit F2
24	0.42	0.16	0.290	0.61	1.03	0.820	0.55	0.66	0.605	
25	0.69	0.66	0.675	1.12	0.92	1.02	0.90	0.82	0.860	
26	0.47	0.50	0.485	0.72	0.78	0.75	0.74	0.69	0.715	
27	0.60	0.62	0.610	1.47	1.20	1.33	0.89	0.80	0.845	
28	— [c]	0.31	0.16	— [c]	0.41	— [c]	— [c]	0.35	0.18	
29	0.80	0.82	0.810	0.69	0.93	0.810	0.78	0.56	0.670	
30	0.48	0.43	0.455	0.33	0.50	0.415	0.41	0.37	0.390	
31	0.70	0.93	0.815	0.62	0.69	0.655	0.83	0.39	0.610	
32	0.57	0.43	0.500	0.49	0.64	0.565	0.45	0.84	0.645	

Fluoride - mg/l ± 0.01 mg/l
Calibrated Range = 0.00-0.25 mg/l

EVENT #	A1	A2	A av.	F1	F2	F av.	S1	S2	S av.	COMMENTS
1	0.16	0.15	0.155	0.17	0.16	0.165	0.15	0.16	0.155	
2	0.05	0.05	0.05	0.06	0.06	0.06	0.05	0.06	0.055	
3	0.06	a	0.06	0.08	0.08	0.08	0.07	0.21	0.14	
4	b	b	b	b	b	b	0.19	0.22	0.205	
5	b	b	b	b	b	b	b	b	b	
6	b	b	b	b	b	b	b	b	b	
7	0.05		0.05	0.04	0.04	0.04	0.04	0.03	0.035	
8	0.02	a	0.02	0.04	0.05	0.045	0.03	0.03	0.03	
9	<0.01	a	<0.01	0.01	0.01	0.01	<0.01	0.01	0.01	
10	c	a	a + c	0.01	0.04	0.025	c	<0.01	0.01	
11	0.12	0.10	0.11	0.18	0.04	0.11	0.10	0.11	0.105	
12	0.05	0.05	0.05	0.09	0.05	0.07	0.06	0.05	0.055	
13	b	b	b	b	b	b	b	b	b	
14	0.04	0.05	0.045	0.03	0.02	0.05	0.02	0.04	0.03	
15	0.11	0.08	0.095	0.09	0.06	0.075	0.09	0.10	0.095	
16	0.02	0.02	0.045	0.04	0.03	0.035	0.02	0.02	0.02	
17	0.10	0.12	0.11	0.12	0.11	0.115	0.14	0.14	0.14	
18	f	f	f	0.03	0.02	0.025	0.04	0.04	0.04	
19	0.11	0.11	0.11	e	0.13	0.13	0.21	0.24	0.225	
20	0.08	0.08	0.08	0.11	0.17	0.14	0.15	0.15	0.15	
21	0.19	0.17	0.18	0.20	0.12	0.16	0.14	0.14	0.145	
22	0.30	0.26	0.28	0.44	0.40	0.42	0.25	0.25	0.25	
23	0.08	0.07	0.075	0.26	0.19	0.225	0.16	0.14	0.15	
24	0.31	0.31	0.31	0.40	0.46	0.43	0.40	0.39	0.395	
25	0.08	0.06	0.07	0.09	0.08	0.085	0.09	0.06	0.075	
26	0.08	0.07	0.075	0.10	0.10	0.10	0.11	0.10	0.105	
27	0.14	0.11	0.125	0.15	0.18	0.165	0.14	0.11	0.125	
28	0.04	0.05	0.045	0.05	0.06	0.055	0.05	0.05	0.05	
29	0.16	0.15	0.155	0.13	0.19	0.115	0.14	0.14	0.14	
30	0.06	0.08	0.07	0.09	0.13	0.11	0.09	0.08	0.085	
31	0.12	0.16	0.14	0.11	0.12	0.115	0.15	0.09	0.12	
32	0.08	0.04	0.06	0.07	0.10	0.085	0.03	0.09	0.06	

Precision: 15 μsiemens ± .05
50 " ± .2
150 " ± .5
500 " ± 1

Conductivity-μsiemens

EVENT #	A1	A2	A av.	F1	F2	F av.	S1	S2	S av.	COMMENTS
1	____b	____b	____b	56.0	____	56.0	64.2	73.0	68.6	Insufficient A1,A2,F2 Small F1,S1,S2
2	70.0	69.8	69.9	69.6	71.8	70.7	72.6	72.6	72.5	
3	77.0	____a	77.0	143.0	213	178.	72.4	191.	45.8	Particulates in F1,F2,S2
4	____a	____a	____a	____b	____b	____b	____b	____b	____b	Insufficient S1,S2
7	____a	____a	____a	____b	____b	____b	77.8	38.5	58.2	Insufficient A1,A2,F1,F2 Particulates in S1,S2-esp.S
8	33.2	____a	33.2	35.8	28.3	32.1	35.6	36.3	36.0	
9	15.9	____a	15.9	14.5	10.3	12.4	14.0	14.0	13.7	
10	9.52	____a	9.52	7.04	8.64	7.84	12.8	12.5	12.6	
11	16.3	161.	162.	153.	47.3	100.	148.	152.	150.	F2 checked
12	57.5	53.8	55.7	54.0	57.5	55.8	48.1	45.5	46.8	
14	49.3	48.9	49.1	49.6	47.4	48.5	49.8	49.3	50.0	
15	38.4	37.7	38.1	28.5	39.1	33.8	22.9	37.3	30.1	F1S1 checked
16	26.0	26.3	26.2	19.8	26.3	23.1	22.7	12.4	17.6	
17	63.8	58.2	61.0	62.3	63.4	62.5	62.1	55.7	58.9	
18	____b	____b	____b	21.1	22.2	21.7	20.6	20.2	20.4	
19	79.7	71.9	75.8	70.5	55.0	62.75	72.2	74.0	73.1	A1 A2 small
20	71.8	71.0	71.0	66.0	37.2	51.6	52.0	52.0	52.0	
21	____b	____b	____b	70.2	61.8	66.0	45.6	52.3	49.0	Insufficient A1,A2 Small Volume F1,F2
22	48.4	54.2	51.3	65.4	52.2	58.8	68.4	77.5	73.0	
23	36.2	38.0	37.1	35.9	29.3	32.6	37.8	36.3	38.0	
24	74.5	66.5	70.5	84.5	82.0	83.2	79.0	76.0	77.5	
25	43.2	44.9	44.1	53.8	48.7	51.3	48.3	48.0	48.2	
26	61.0	59.0	60.0	63.8	67.3	65.6	69.0	68.2	379.	
27	____b	____b	____b	69.8	62.3	66.1	52.5	56.2	54.4	Small sample F2 Insufficient A1,A2
28	22.7	22.8	22.8	20.3	23.9	22.1	21.6	19.7	20.7	
29	43.6	46.3	45.0	38.6	45.7	42.2	32.3	22.9	27.6	Small sample A1
30	21.1	21.9	21.5	24.1	25.4	24.3	19.7	20.4	20.1	
31	19.6	22.3	20.9	23.1	25.4	24.3	21.6	25.2	23.4	
32	40.9	38.8	39.9	38.3	39.9	39.1	43.9	43.8	43.9	

Calcium - mg/l ±0.03 mg/l

EVENT #	A1	A2	A av.	F1	F2	F av.	S1	S2	S av.	COMMENTS
1	___e	3.14	3.14	7.14	5.69	3.91	7.90	9.42	8.66	A1 insufficent sample to rerun particulates in F1,F2,S1,S2.
2	0.50	0.45	0.475	0.54	0.46	.50	0.42	0.42	0.42	
3	0.72	___a	0.72	2.66	2.911	2.91	2.87	1.83	2.35	Particulates F1,F2,S1,S2
4	___b	___b	___b	___b	___b	___b	7.06	8.33	7.69	Particulates S1,S2
5	___b	___b	___b	___b	___b	___b	___b	___b	___b	
6	___b	___b	___b	___b	___b	___b	___b	___b	___b	
7	___b	0.81	0.81	2.44	2.06	2.25	3.55	3.79	3.67	S1,S2 Particulates
8	2.70	___a	2.70	3.21	2.63	2.92	3.42	3.39	3.40	
9	0.24	___a	0.24	0.36	2.73	1.54	0.56	0.39	0.475	F2 contaminated
10	0.21	___a	0.21	0.24	0.21	0.22	0.21	0.21	0.210	
11	0.52	0.65	0.585	1.63	0.43	1.03	1.50	1.18	1.34	F1 has bugs
12	0.35	0.29	0.32	1.02	0.74	0.88	1.38	1.45	1.42	S1,S2 have bugs& particulate
13	___b	___b	___b	___b	___b	___b	___b	___b	___b	
14	0.29	0.29	0.29	0.46	0.40	0.43	0.32	0.32	0.320	
15	0.77	0.82	0.795	0.82	1.03	0.925	0.64	0.88	0.76	
16	0.33	0.32	0.325	0.60	0.26	0.43	0.29	0.27	0.28	
17	0.40	0.25	0.325	0.85	0.77	0.81	1.04	1.22	1.13	
18	___f	___f	___f	0.46	0.31	0.385	0.26	0.44	0.35	
19	0.37	0.51	0.44	1.08	1.95	1.51	1.66	1.59	1.63	
20	1.19	1.32	1.25	3.28	___e	3.28	3.92	3.97	3.05	F1,F2,S1,S2,bugs & particulates
21	2.08	2.19	2.135	6.30	3.14	4.72	5.55	5.57	5.56	S2 - Bugs
22	1.78	1.99	1.885	6.78	5.94	6.36	___e	___e	___e	F1,F2,S1,S2 Black Particulat and bugs
23	0.57	0.59	0.58	1.46	1.93	1.695	0.72	0.85	7.85	R = 1.35
24	0.66	0.75	0.705	1.59	1.74	1.665	1.47	1.33	1.35	
25	0.54	0.56	0.55	1.20	0.96	1.08	0.85	0.92	0.885	
26	0.49	0.65	0.57	1.35	1.22	1.285	1.20	1.27	1.24	
27	0.61	0.46	0.535	2.97	2.23	2.60	3.54	3.54	3.54	
28	0.46	0.44	0.45	0.76	0.69	0.725	0.65	0.73	0.69	
29	1.01	1.01	1.01	1.12	1.21	1.17	1.16	0.96	1.06	
30	0.03	0.005	0.018	0.78	0.74	0.76	0.53	0.52	0.525	R_F 43.4, RS = 30
31	0.52	0.34	0.43	0.64	0.46	0.55	0.96	0.62	0.79	
32	0.48	0.51	0.495	1.09	1.14	1.115	1.02	1.11	1.07	

Magnesium - mg/l ± 0.01 mg/l

EVENT #	A1	A2	A av.	F1	F2	F av.	S1	S2	Sav.	COMMENTS
1	0.34	0.28	0.31	0.52	0.46	0.49	1.01	1.07	1.04	
2	0.02	0.01	0.015	0.05	0.04	0.045	0.02	0.04	0.03	
3	0.09	a	0.09	0.70	1.00	0.85	0.50	0.64	0.57	
4	b	b	b	b	b	b	0.73	0.73	0.73	
5	b	b	b	b	b	b	b	b	b	
6	b	b	b	b	b	b	b	b	b	
7	b	0.10	0.10	0.59	0.45	0.52	0.98	0.81	0.895	
8	0.43	a	0.43	0.43	0.39	0.41	0.38	0.38	0.38	
9	0.01	a	0.01	0.05	0.81	0.43	0.09	0.05	0.07	
10	0.02	a	0.02	0.02	0.04	0.03	0.01	0.02	0.015	
11	0.02	0.07	0.045	0.29	0.25	0.50	0.40	0.24	0.32	
12	0.06	0.05	0.055	0.08	0.07	0.075	0.11	0.15	0.13	
13	b	a	a + b	b	b	b	b	b	b	
14	0.05	0.05	0.05	0.09	0.09	0.09	0.05	0.06	0.055	
15	0.07	0.09	0.08	0.07	0.13	0.10	0.05	0.07	0.06	
16	~0.02	<0.01	0.015	0.07	<0.01	0.04	<0.01	<0.01	0.01	
17	0.04	<0.01	0.025	0.13	0.15	0.14	0.17	0.33	0.25	
18	f	f	f	0.09	0.05	0.07	0.01	0.03	0.02	
19	0.08	0.12	0.10	0.29	0.47	0.38	0.50	0.50	0.50	
20	0.20	0.22	0.21	0.65	2.90	1.775	0.66	0.73	0.695	F2(bug) S1,S2 (particulates
21	0.31	0.29	0.30	1.55	0.39	0.97	0.94	0.93	0.935	
22	0.33	0.35	0.34	1.30	1.06	1.18	3.19	2.11	2.65	F1,F2,S1,S2 contaminated with bugs & particulates.
23	0.06	0.04	0.05	0.29	0.52	0.405	0.08	0.12	0.10	
24	0.06	0.08	0.07	0.23	0.38	0.305	0.24	0.25	0.245	
25	0.08	0.09	0.085	0.30	0.26	0.28	0.19	0.21	0.20	
26	0.03	0.06	0.045	0.25	0.17	0.21	0.13	0.17	0.15	
27	<0.01	<0.01	0.01	0.50	0.35	0.425	0.55	0.52	0.51	
28	0.09	0.08	0.085	0.17	0.13	0.15	0.12	0.16	0.14	
29	0.16	0.15	0.155	0.23	0.21	0.22	0.29	0.22	0.255	
30	<0.01	<0.01	0.01	0.09	0.12	0.105	0.03	0.08	0.055	
31	0.08	0.03	0.055	0.11	0.06	0.085	0.10	0.05	0.075	
32	<0.01	0.05	0.03	0.12	0.11	0.23	0.10	0.09	0.095	

Sodium - mg/l ± .01 mg/l

Calibrated Range 0.00-1.00 mg/l

EVENT #	A1	A2	A av.	F1	F2	F av.	S1	S2	S av.	COMMENTS
1	1.04	0.64	0.84	0.28	1.14	0.71	0.30	0.37	0.30	
2	0.06	0.10	0.08	0.35	0.12	0.235	0.06	0.06	0.06	
4	[b]	[b]	[b]	[b]	[b]	[b]	1.00	1.51	1.255	
5	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	
6	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	
7	0.09	0.11	1.0	0.08	0.11	0.095	0.29	0.09	0.19	
8	0.04	[a]	0.04	0.22	0.13	0.175	0.06	0.13	0.095	
9	0.04	[a]	0.04	0.11	0.69	0.40	0.06	0.06	0.06	
10	0.09	[a]	0.09	0.37	1.73	1.05	0.10	0.10	0.10	
11	0.07	0.06	0.065	0.10	0.13	0.115	0.08	0.08	0.08	
12	0.02	0.02	0.02	0.62	0.02	0.32	0.09	0.09	0.09	
13	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	
14	0.02	0.02	0.02	0.04	0.13	0.085	0.02	0.02	0.02	
15	0.07	0.07	0.07	0.04	0.04	0.04	0.05	0.03	0.04	
16	0.05	0.04	0.045	0.86	0.23	0.545	0.06	[c]	0.06	
17	0.05	0.06	0.055	0.10	0.08	0.09	0.06	0.07	0.065	
18	[f]	[f]	[f]	0.15	0.06	0.105	0.07	0.05	0.06	
19	0.08	0.08	0.08	[e]	0.19	0.19	0.53	0.19	0.36	
20	0.27	0.28	0.275	0.45	1.08	0.765	0.34	0.32	0.33	
21	0.64	0.58	0.61	0.66	0.44	0.55	0.52	0.60	0.56	
22	0.38	0.42	0.40	1.16	0.70	0.93	0.74	0.83	0.785	
23	0.02	0.01	0.15	0.34	0.79	0.565	0.01	0.03	0.02	
24	0.02	< 0.01	0.015	0.07	0.45	0.26	0.12	0.07	0.095	
25	0.24	0.25	0.245	0.50	0.34	0.42	0.30	0.31	0.305	
26	0.08	0.10	0.09	0.18	0.14	0.16	0.11	0.10	0.105	
27	0.22	0.18	0.02	0.54	0.46	0.50	0.89	0.72	0.805	
28	0.06	0.06	0.06	0.45	0.17	0.31	0.02	0.20	0.11	
29	0.15	0.11	0.13	0.57	0.41	0.49	0.41	0.38	0.395	
30	0.17	0.15	0.16	0.16	0.23	0.195	0.28	0.28	0.28	
31	0.15	0.14	0.145	0.17	0.18	0.175	0.19	0.14	0.165	
32	0.09	0.11	0.10	0.22	0.57	0.395	0.14	0.10	0.12	

Potassium - mg/l ± .01 mg/l   Calibrated Range 0.00-0.50 mg/l

EVENT #	A1	A2	A av.	F1	F2	F av.	S1	S2	S av.	COMMENTS
1	0.40	0.23	0.315	0.30	d	d	0.30	d	d	
2	c	c	c	0.13	0.12	0.125	0.12	c	0.12	
4	b	b	b	b	b	b	0.47	0.60	0.535	
5	b	b	b	b	b	b	b	b	b	
6	b	b	b	b	b	b	b	b	b	
7	0.10	0.16	0.130	0.13	0.18	0.155	0.18	d	d	
8	0.08	a	0.08	0.11	0.13	0.120	0.10	0.12	0.110	
9	0.04	a	0.04	0.04	0.05	0.045	0.02	< 0.01	0.0125	
10	<0.06	a	0.06	0.06	<0.06	0.060	<0.06	<0.06		
11	0.10	0.10	0.100	0.16	0.12	0.140	0.10	0.08	0.090	
12	0.04	0.02	0.030	0.17	0.04	0.105	0.08	0.11	0.095	
13	b	b	b	b	b	b	b	b	b	
14	0.05	0.05	0.050	0.14	0.04	0.090	0.07	0.04	0.055	
15	0.10	0.09	0.095	0.08	0.06	0.070	0.09	0.05	0.070	
16	0.07	0.06	0.065	0.25	0.26	0.025	0.07	0.06	0.065	
17	0.11	0.11	0.110	0.22	0.13	0.175	0.12	0.13	0.125	
18	f	f	f	0.43	0.06	0.245	0.08	0.08	0.080	
19	0.10	0.07	0.085	0.59	0.14	0.365	0.38	0.12	0.25	
20	0.03	0.04	0.035	0.31	0.52	0.415	0.12	0.09	0.105	
21	0.23	0.15	0.190	0.29	0.21	0.245	0.25	0.33	0.290	
22	0.12	0.11	0.115	0.74	0.24	0.490	0.30	0.33	0.315	
23	0.03	0.04	0.035	0.19	0.33	0.260	0.03	0.04	0.035	
24	0.09	0.05	0.070	0.24	0.46	0.350	0.09	0.09	0.090	
25	<0.01	<0.01	<0.01	0.26	0.10	0.180	0.01	0.04	0.025	
26	0.03	0.08	0.055	0.26	0.13	0.195	0.05	0.03	0.030	
27	0.72	0.19	0.455	0.75	0.55	0.650	0.34	2.04	0.793	
28	<0.01	b	0.005	0.12	0.14	0.130	0.01	0.21	0.110	omit A_2
29	0.08	0.03	0.055	0.08	0.29	0.185	0.08	0.12	0.100	
30	0.05	0.06	0.055	0.09	0.14	0.115	0.06	0.05	0.055	
31	0.05	0.08	0.065	0.08	0.08	0.080	0.31	0.03	0.170	
32	0.03	0.08	0.055	0.08	0.26	0.170	0.02	0.02	0.02	

<u>Volume (ml)</u>

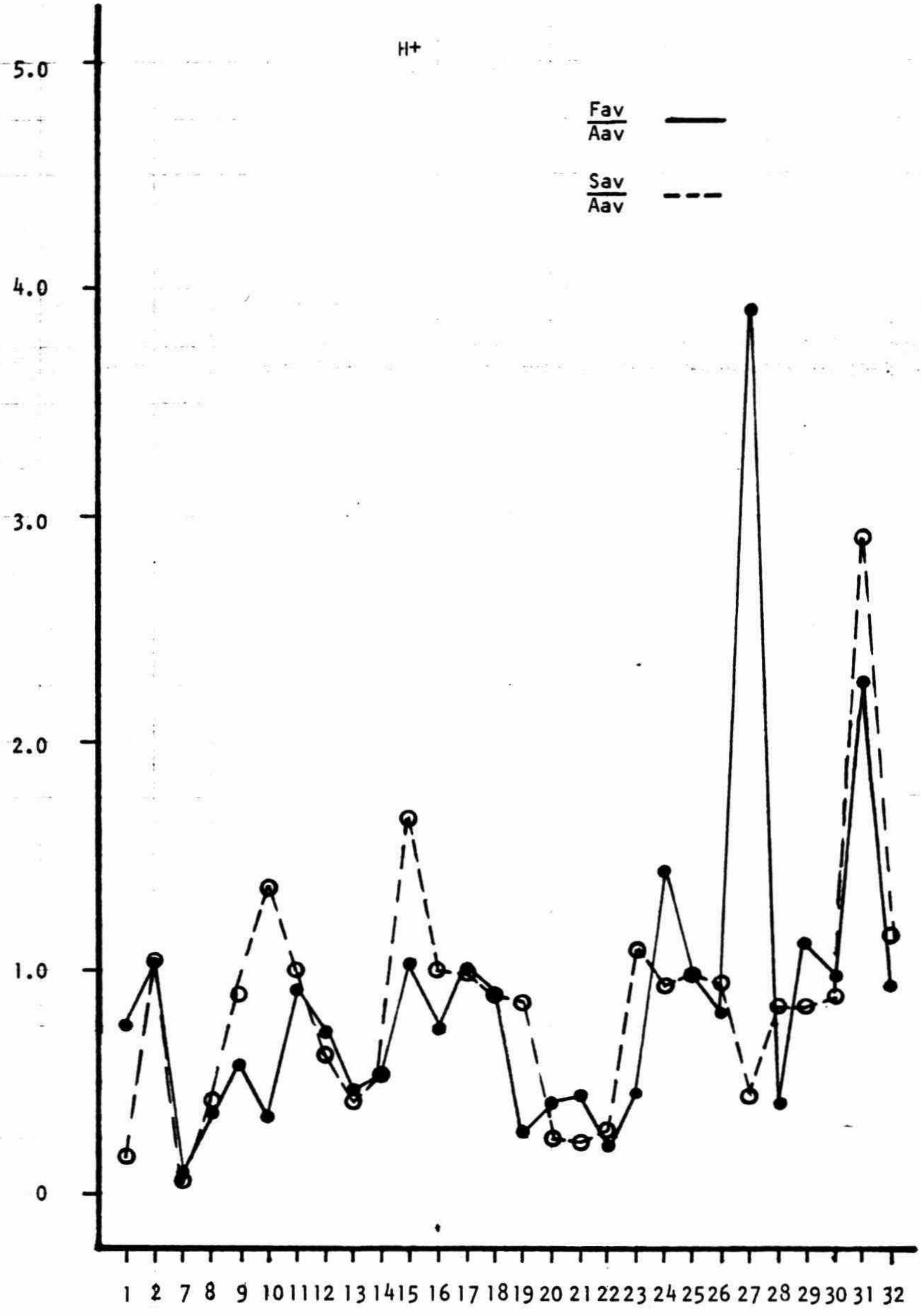
EVENT #	A1	A2	A av.	F1	F2	F av.	S1	S2	S av.	COMMENTS
1	21.9	24.0	23.0	59.6	58.1	58.9	108.3	107.5	107.9	
2	2536	2479	2508	4350*	4350*	4350	6300	6415	6358	*estimated due to overfil
3	100.2	-	100.2	199	203	201	309	307	308	
4	-	-	-	-	-	-	32.8	27.7	30.3	
5	-	-	-	-	-	-	5.8	11.5	8.7	
6	-	-	-	-	-	-	11.7	10.1	10.9	
7	32.7	29.0*	30.9	59.0	79.8	69.4	111.3	112.2	111.8	*A2 left open for 24 hrs.
8	208	-	208	339	343	341	541	569	555	
9	1942	-	1942	3504	3485	3495	5148	4986	5067	
10	614	-	614	1104	984	1044	998	924	961	
11	766	750	758	1431*	1317	1374	1892	1946	1919	
12	196	185	191	372*	337	355	488	494	491	
13	13.5	3.7	8.6	10.7*	15.1	12.9	63.9	72.4	68.2	
14	1361	1285	1323	2883*	2389	2636	3418	3483	3451	
15	618	616	617	1099	1109	1104	1625	1691	1658	
16	260+	994	994	2120*	1893	2007	2690	2646	2668	+lost in spill *Fl(b)
17	421	357	389	862	835	849	1151*	1079*	1115	*many small flies Fl(b)
18	179	196	188	361	326	344	526	519	523	
19	70	66	68	146	104	125	213	219	216	
20	118	124	121	237	245	241	326	295	311	
21	26	24	25	41	54	48	100	70+	85	+lots of flies Fl and 2b
22	43	43	43	98	70	84+	116x	121x	119	x dark part icles
23	184	190	187	463	420	442	497	494	496	
24	225	227	226	555	565	560	594	637	616	
25	374	386	380	833	754	794	1096	1082	1089	
26	255	224	240	722	563	643	845	830	838	
27	18.5	23.3	20.9	64.3	48.1	56.2	89.1	87.5	88.3	
28	820	795	808	1973	1623	1798	1999	2136	2068	
29	67	67	67	291	371	331	-*	-*	-*	*sample "spilled out"
30	541	546	544	1051	1219	1135	1419	1488	1454	
31	77	84	81	156	179	168	185	198	192	
32	580	559	570	1190	1212	1201	1304	1324	1314	

Rainfall Recovery (mm)

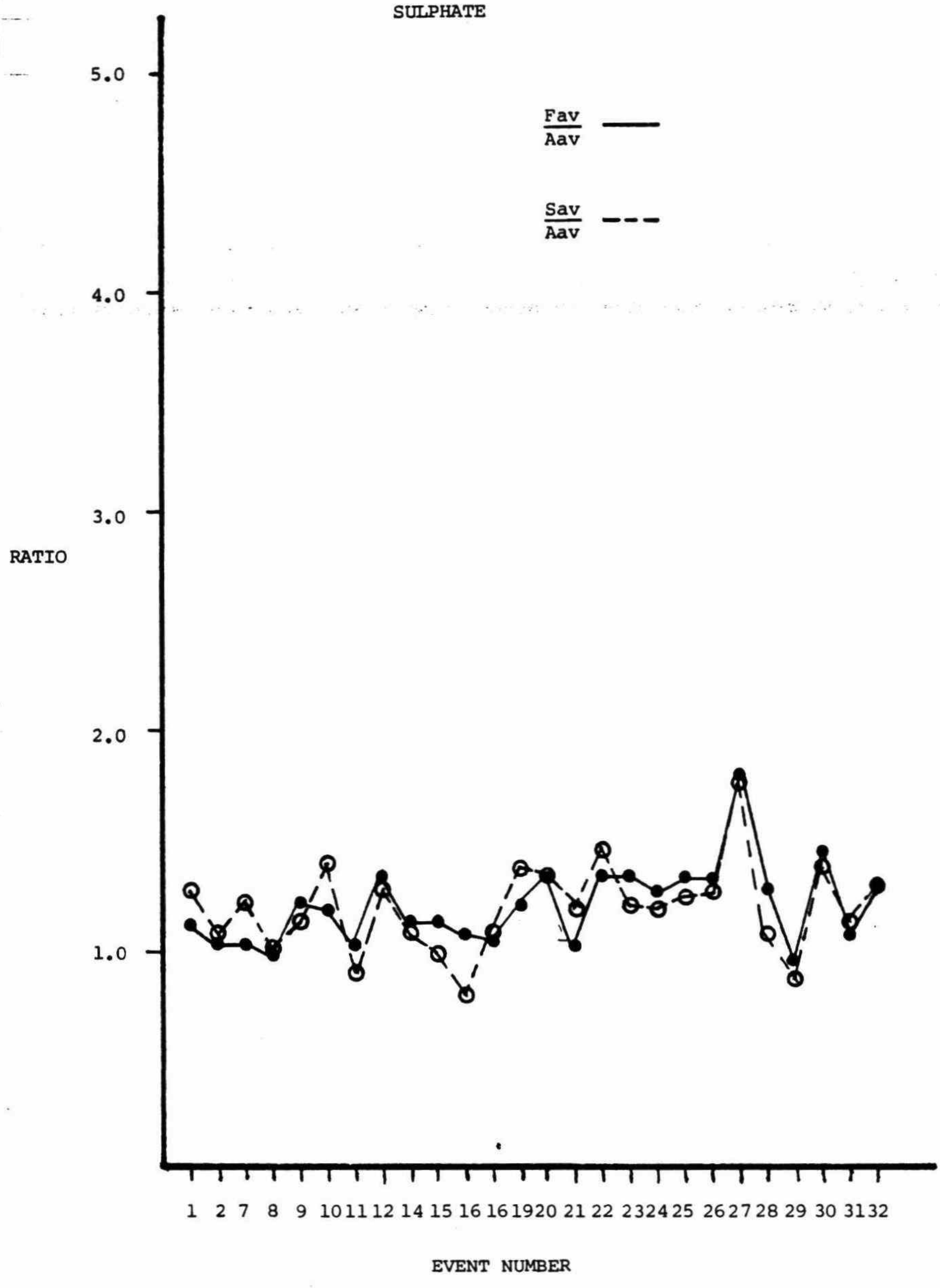
EVENT #	A1	A2	A av.	F1	F2	F av.	S1	S2	S av.	COMMENTS
1	0.4	0.4	0.4	0.5	0.5	0.5	0.7	0.7	0.7	
2	46.0	39.1	39.6	36.8	36.8	36.8	39.6	40.3	40.0	
3	1.6	-	1.6	1.7	1.7	1.7	1.9	1.9	1.9	
4	-	-	-	-	-	-	0.2	0.2	0.2	
5	-	-	-	-	-	-	-	0.1	0.1	
6	-	-	-	-	-	-	0.1	0.1	0.1	
7	0.5	0.5	0.5	0.5	0.7	0.6	0.7	0.7	0.7	
8	3.3	-	3.3	2.9	2.9	2.9	3.4	3.6	3.5	
9	30.6	-	30.6	29.7	29.5	29.6	32.4	31.4	31.9	
10	9.7	-	9.7	9.3	8.3	8.8	6.3	5.8	6.0	
11	12.1	11.8	12.0	12.1	11.1	11.6	11.9	12.2	12.1	
12	3.1	2.9	3.0	3.2	2.9	3.0	3.1	3.1	3.1	
13	0.2	0.1	0.15	0.1	0.1	0.1	0.4	0.5	0.4	
14	21.5	20.3	20.9	24.4	20.2	22.3	21.5	21.5	21.7	
15	9.8	9.7	9.7	9.3	9.4	9.3	10.2	10.6	10.4	
16	4.1	15.7	15.7	17.9	16.0	17.0	16.9	16.6	16.8	
17	6.6	5.6	6.1	7.3	7.1	7.2	7.2	6.8	7.0	
18	2.6	3.1	3.0	3.1	2.8	2.9	3.3	3.3	3.3	
19	1.1	1.0	1.1	1.2	0.9	1.1	1.3	1.4	1.4	
20	1.9	2.0	1.9	2.0	2.1	2.0	2.1	1.9	2.0	
21	0.4	0.4	0.4	0.4	0.5	0.4	0.6	0.4	0.5	
22	0.7	0.7	0.7	0.8	0.6	0.7	0.7	0.8	0.8	
23	2.9	3.0	3.0	3.9	3.6	3.7	3.1	3.1	3.1	
24	3.6	3.6	3.6	4.7	4.8	4.7	3.7	4.0	3.9	
25	5.8	6.1	5.95	7.1	6.4	6.75	6.9	6.8	6.85	
26	4.0	3.5	3.75	6.1	4.8	5.45	5.3	5.2	5.25	
27	0.3	0.4	0.35	0.5	0.4	0.45	0.6	0.6	0.6	
28	12.9	12.9	12.9	16.7	13.7	15.2	12.6	13.4	13.0	
29	1.1	1.1	1.1	2.5	3.1	2.8	-	-	-	
30	8.5	8.6	8.55	8.9	10.3	9.6	8.9	9.4	9.15	
31	1.2	1.3	1.25	1.3	1.5	1.4	1.2	1.3	1.25	
32	9.2	8.8	9.0	10.1	10.2	10.15	8.2	8.3	8.25	

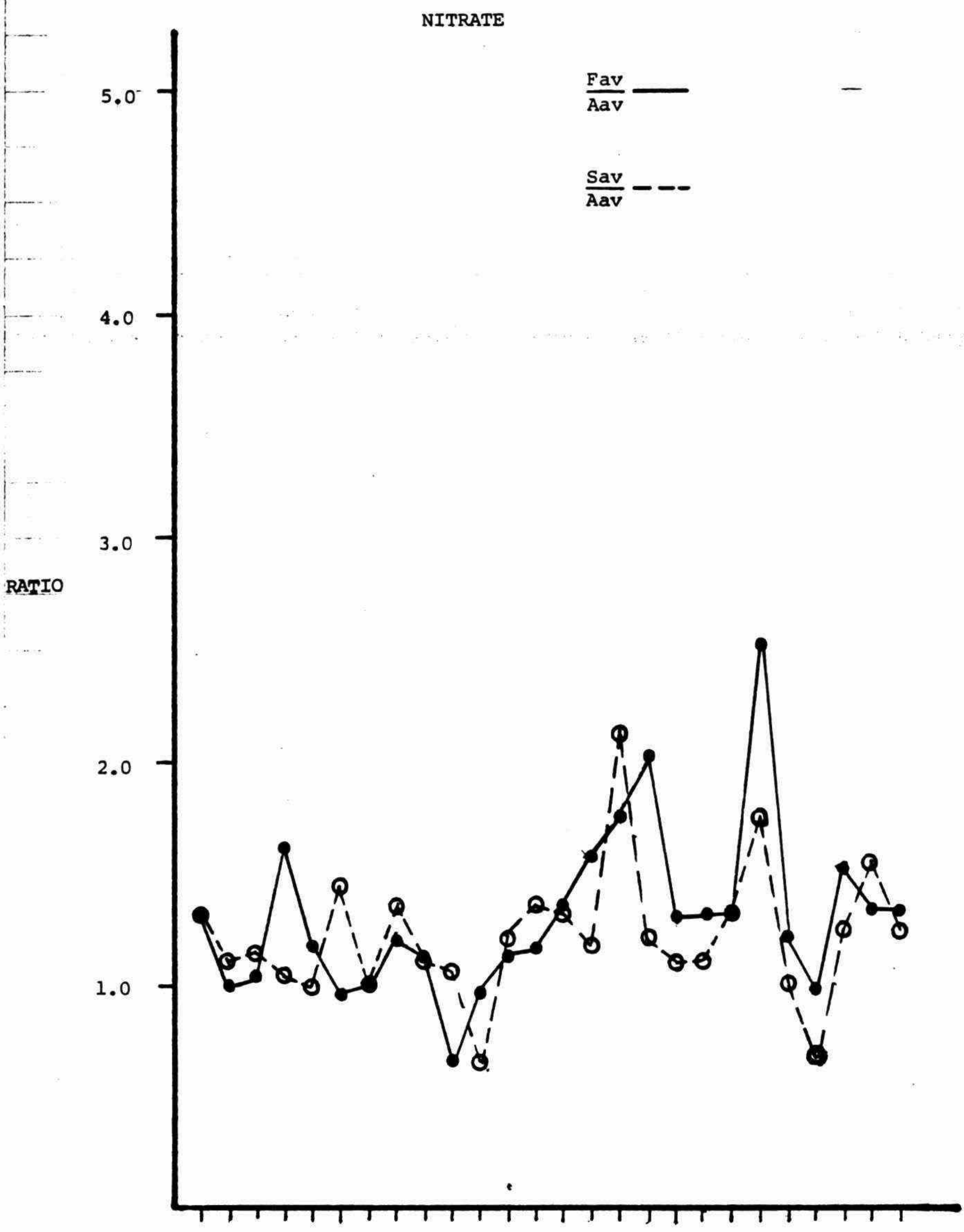
Appendix B

Parameter Ratio Plots

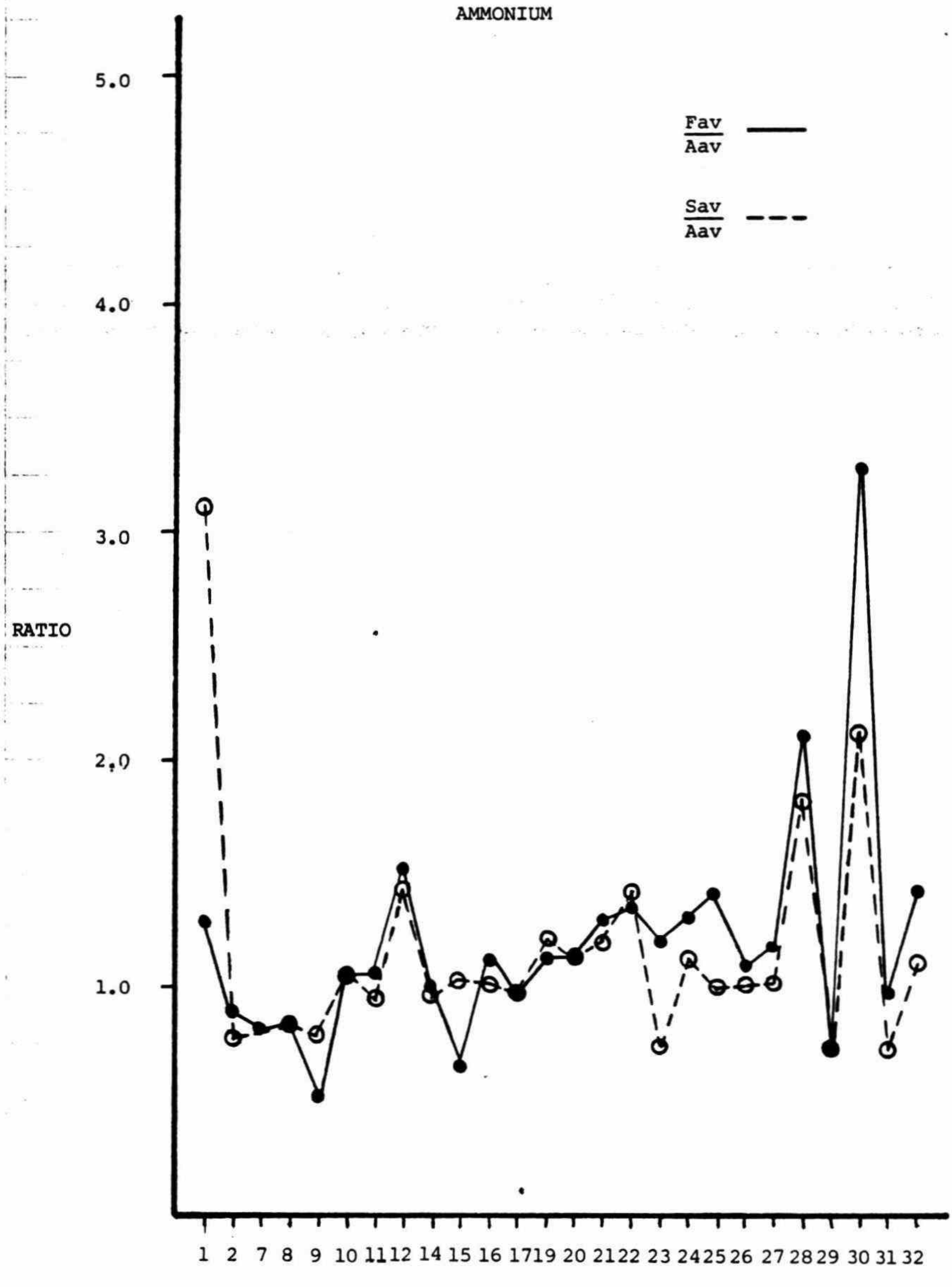

H+
Fav/Aav
Sav/Aav
5.0
4.0
3.0
2.0
1.0
0
1 2 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32

1234 3

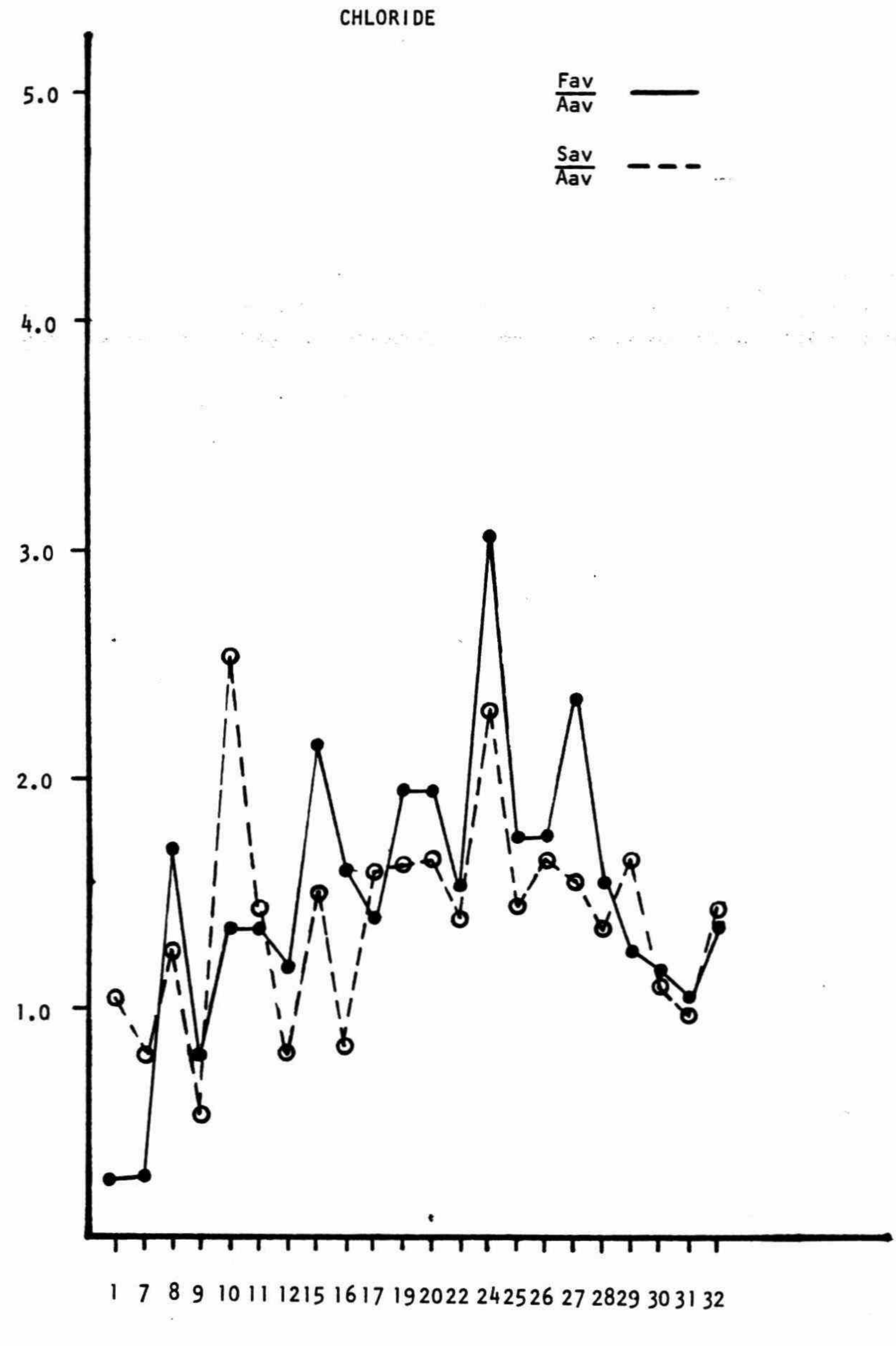

SULPHATE
5.0
4.0
3.0
2.0
1.0
RATIO
Fav/Aav
Sav/Aav
1 2 7 8 9 10 11 12 14 15 16 16 19 20 21 22 23 24 25 26 27 28 29 30 31 32
EVENT NUMBER

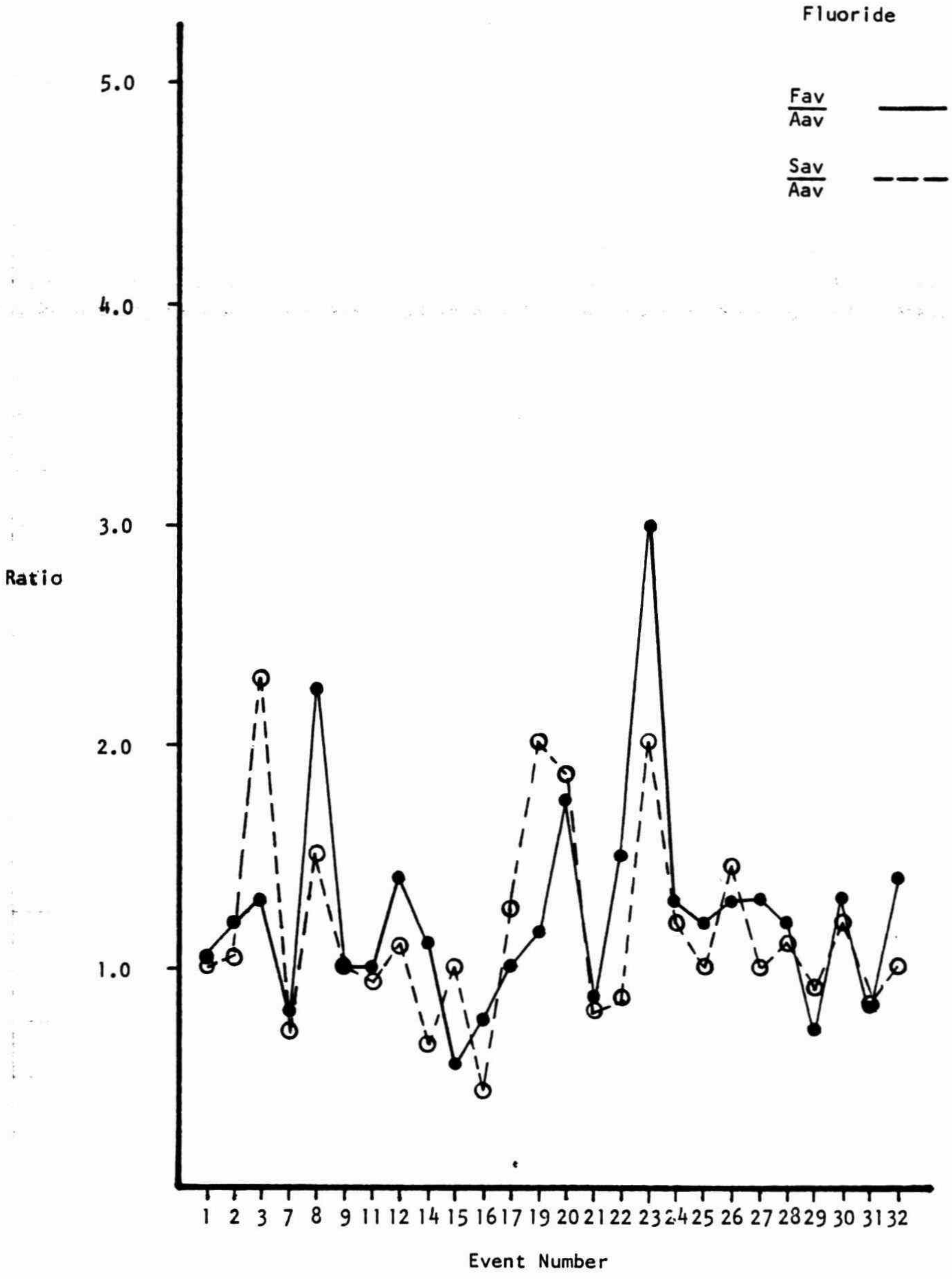


NITRATE
Fav/Aav
Sav/Aav
5.0
4.0
3.0
2.0
1.0
RATIO
1 2 7 8 9 10 11 12 14 15 16 17 19 20 21 22 23 24 25 26 27 28 29 30 31 32
EVENT NUMBER



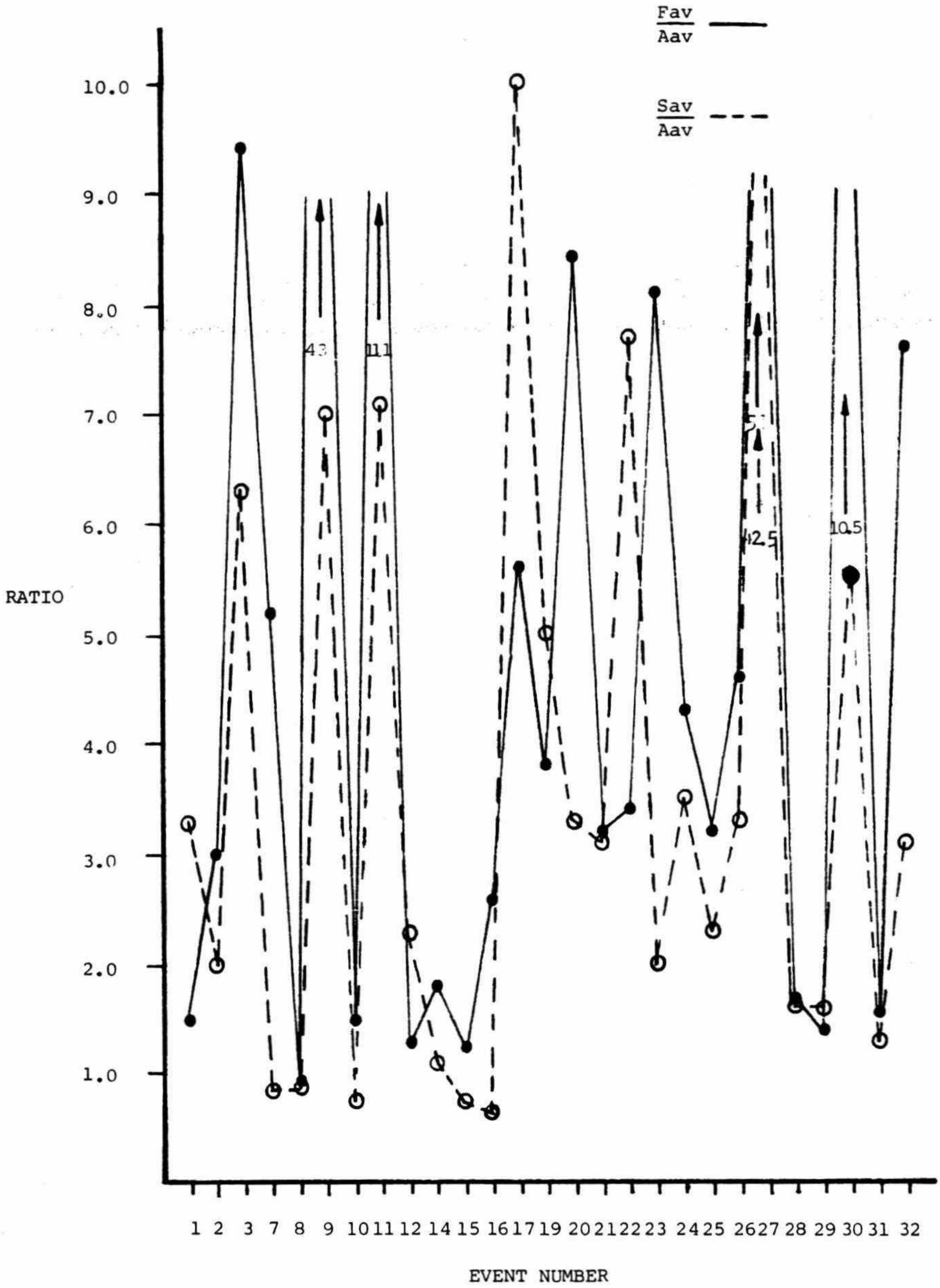
AMMONIUM
Fav / Aav
Sav / Aav
RATIO
5.0
4.0
3.0
2.0
1.0
1 2 7 8 9 10 11 12 14 15 16 17 19 20 21 22 23 24 25 26 27 28 29 30 31 32
EVENT NUMBER


CHLORIDE
Fav/Aav
Sav/Aav
5.0
4.0
3.0
2.0
1.0
1 7 8 9 10 11 12 15 16 17 19 20 22 24 25 26 27 28 29 30 31 32

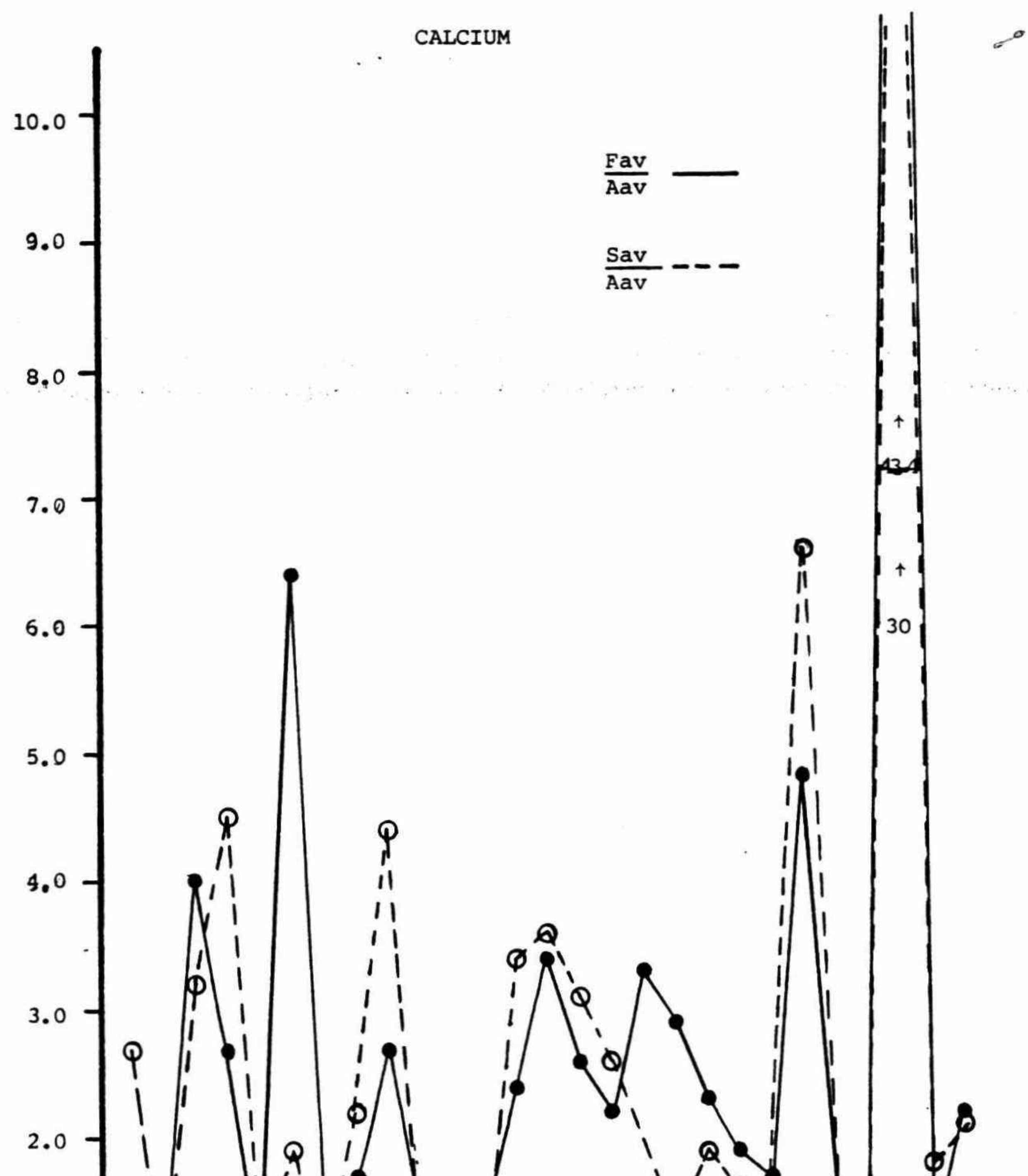


Fluoride
Fav/Aav
Sav/Aav
5.0
4.0
3.0
2.0
1.0
Ratio
1 2 3 7 8 9 11 12 14 15 16 17 19 20 21 22 23 24 25 26 27 28 29 30 31 32
Event Number

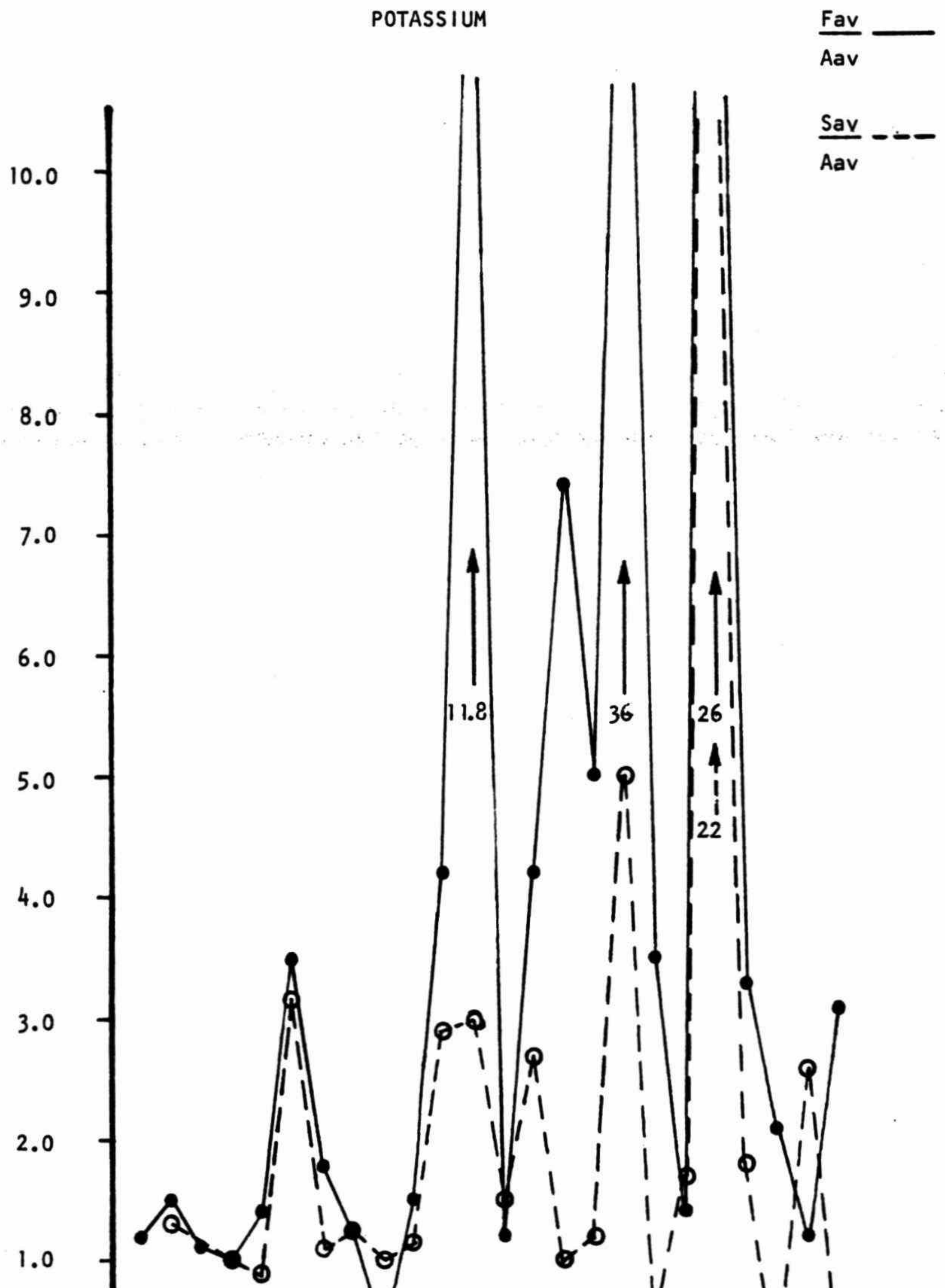
MAGNESIUM



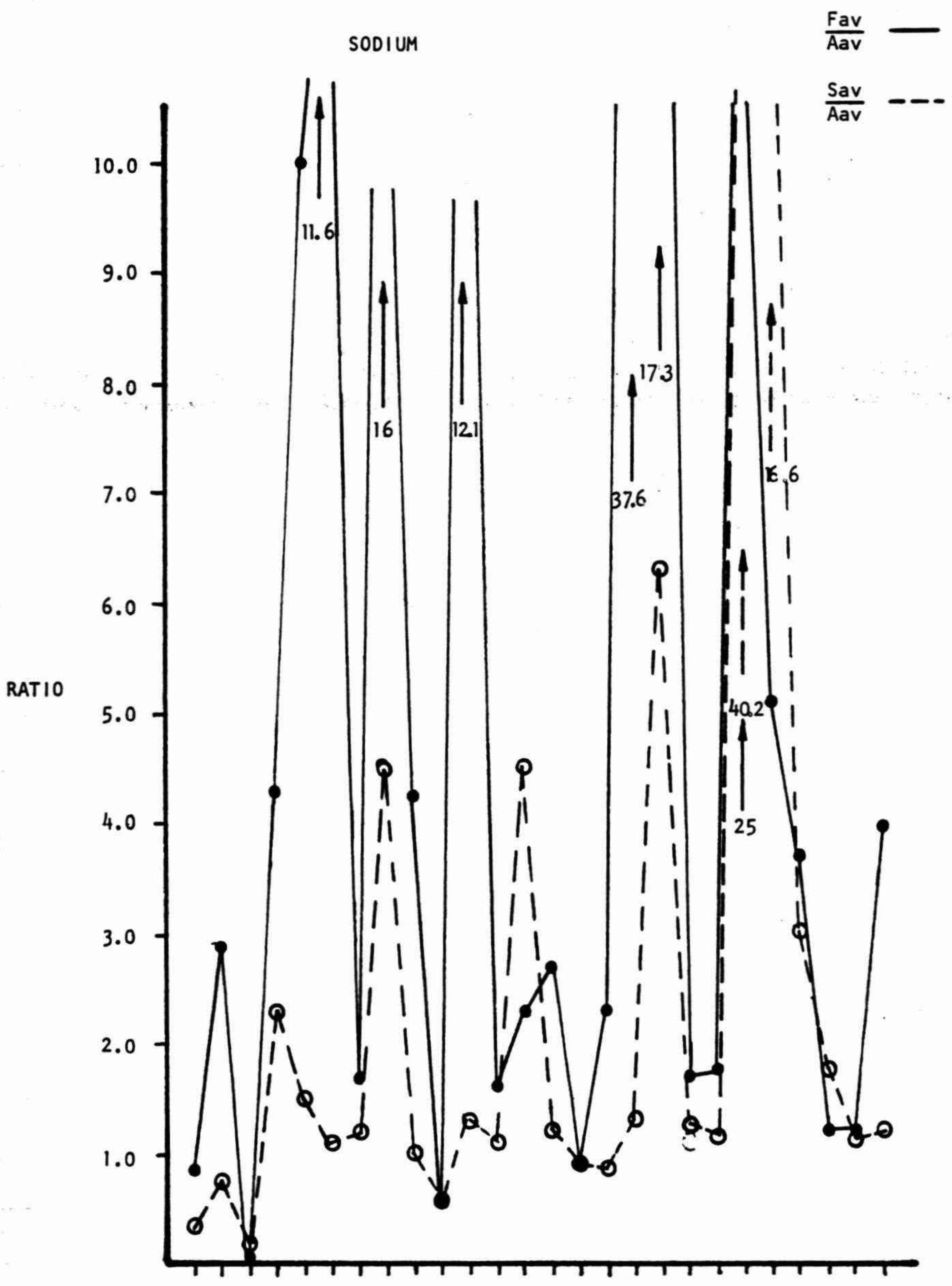
Fav/Aav
Sav/Aav
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
RATIO
43
111
12.5
10.5
1 2 3 7 8 9 10 11 12 14 15 16 17 19 20 21 22 23 24 25 26 27 28 29 30 31 32
EVENT NUMBER



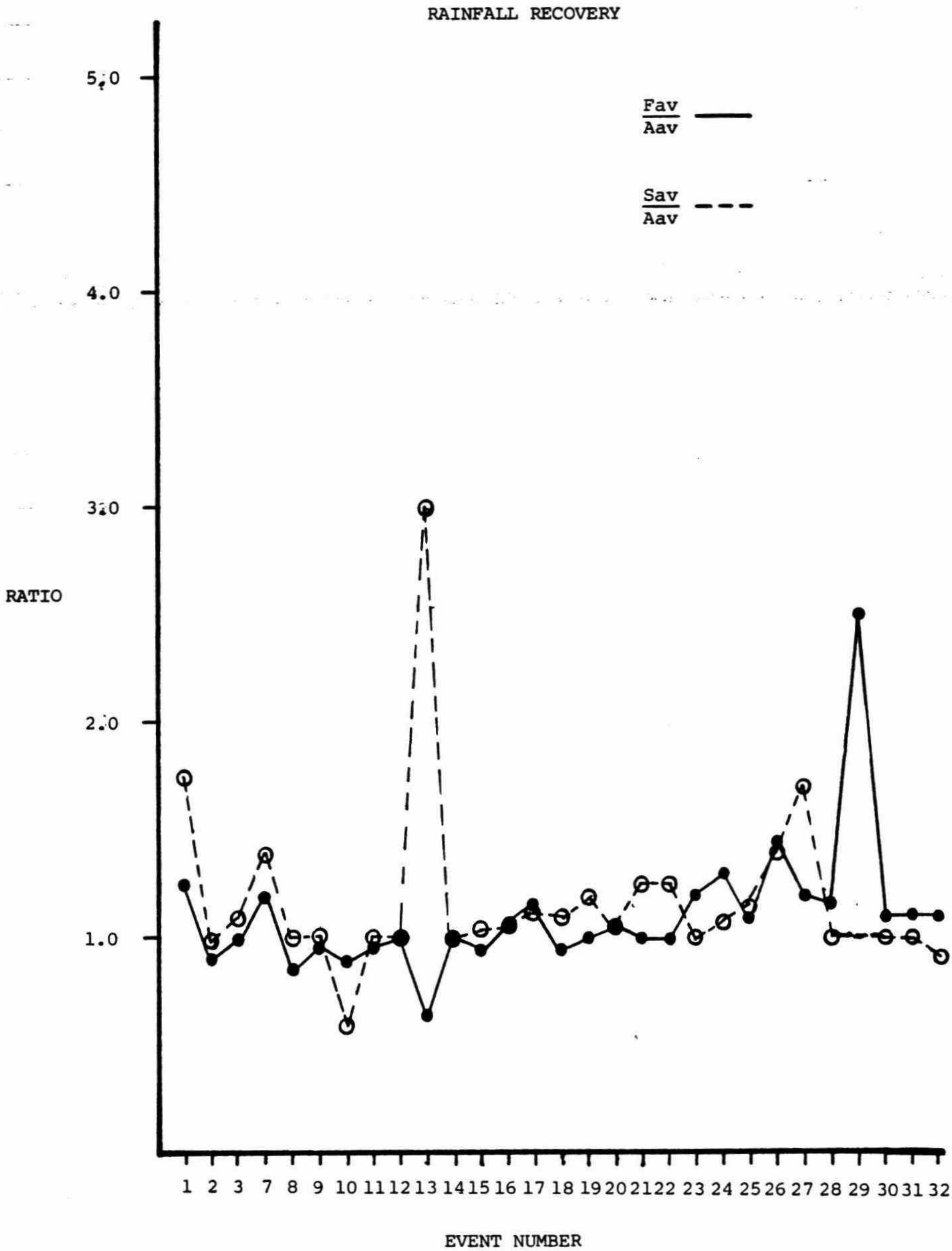
CALCIUM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Fav/Aav
Sav/Aav
43.4
30
1 2 3 7 8 9 10 11 12 14 15 16 17 19 20 21 22 23 24 25 26 27 28 29 30 31 32



POTASSIUM
Fav / Aav
Sav / Aav
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
11.8
36
26
22
7 8 9 10 11 12 14 15 16 17 19 20 21 22 23 24 25 26 27 28 29 30 31 32



SODIUM
Fav/Aav
Sav/Aav
RATIO
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
11.6
16
12.1
37.6
17.3
40.2
25
1 2 7 8 9 10 11 12 14 15 16 17 19 20 21 22 23 24 25 26 27 28 29 30 31 32
EVENT NUMBER


RAINFALL RECOVERY
Fav
Aav
Sav
Aav
5.0
4.0
3.0
2.0
1.0
RATIO
1 2 3 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32
EVENT NUMBER

Appendix C

Statistical Summary Tables

TABLE C1

Variance Within Sampler Types

R ≥ 2.8 mm

		H_3O^+	NO_3^-	SO_4^{-2}	NH_4^+	Cl^-	F^-	Cond.	Ca^{+2}	Mg^{+2}	Na^+	K^+	R
A	S_G	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	T	.65047	1.6268	0	1.1645	0	1.0471	1.7417	.62224	1.1494	.86173	.68024	.14196
	N	15	14	14	13	12	14	14	14	10	13	11	15
F	S_G	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	S
	T	.03221	.11295	1.0429	.15791	1.5030	.85366	.15352	.28038	1.1984	.64697	.78538	2.3588
	N	17	15	17	15	12	18	18	18	17	17	17	17
S	S_G	S	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	T	2.5500	.88852	1.0669	1.0799	.09695	1.0000	1.1019	.48771	1.4680	.39948	.69049	.37838
	N	17	17	17	16	12	16	18	18	17	16	15	17

S = Significant (S) or Not Significant (NS) at 95%
T = Paired T Test Value
N = Number of Events

*NS at 98%

TABLE C2

Variance Between Sampler Types

Rainfall ≥ 2.8 mm

		NH_4^+	K^+	Na^+	Ca^{+2}	Mg^{+2}	Cl^-	Cond.	F^-	H^+	NO_3^-	R	SO_4^{-2}
A & F	S_G	NS	S	S	S	S	S*	NS	S*	NS	S	NS	S
	T	2.0577	3.6602	3.9563	5.2145	4.1412	2.5529	0.7637	2.2133	1.4244	2.8192	1.3609	6.1485
	N	14	14	16	16	16	14	16	15	15	16	17	14
A & S	S_G	NS	NS	NS	NS**	S	NS**	NS	NS**	NS	S	NS	NS
	T	0.09937	0.3013	1.3790	1.8534	3.6471	1.849	0.5895	1.8364	0.8301	3.4032	0.9923	1.6923
	N	14	14	16	16	16	13	16	15	15	16	17	14

S_G = Significant (S) or Not Significant (NS) at 95%
T = Paired T Test Value
N = Number of Events

* Significant at 95% but not at 98%
** Significant at 90% but not at 95%

TABLE C3

Variance Within Sampler Types

R < 2.8 mm

		H_3O^+	NO_3^-	SO_4^{-2}	NH_4^+	Cl^-	F^-	Cond.	Ca^{+2}	Mg^{+2}	Na^+	K^+	R
A	S_G	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	T	1.0456	.33401	1.6260	.41646	.53895	1.0242	.22341	.64811	.60302	1.1950	1.4281	.42857
	N	10	9	8	8	8	8	5	7	7	9	9	10
F	S_G	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	T	.75964	.86113	1.3901	1.3621	.72218	.29609	2.3026	1.8887	.21184	.41323	.95910	.76089
	N	11	10	10	10	10	9	8	9	10	9	9	12
S	S_G	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	T	1.0248	.49557	.69052	.73968	.81080	.78633	.31559	1.2404	1.1836	.01387	.80060	.48507
	N	14	11	10	10	10	10	10	10	11	11	9	13

S = Significant (S) or Not Significant (NS) at 95%
T = Paired T Test Value
N = Number of Events

*NS at 98%

TABLE C4

Variance Between Sampler Types

Rainfall < 2.8 mm

		NH_4^+	K^+	Na^+	Ca^{+2}	Mg^{+2}	Cl^-	Cond.	F^-	H^+	NO_3^-	R	SO_4^{-2}
A & F	S_G	NS	S	NS	S	S	NS	NS	NS	S	S	NS	S
	T	1.6027	3.4284	0.5141	3.9453	3.3586	1.4976	0.6991	1.3685	2.8212	3.4246	1.0825	3.1310
	N	9	8	10	11	11	9	7	11	10	10	12	9
A & S	S_G	NS	S	NS	S	S	NS	NS	NS	S	S*	S	S
	T	1.7557	3.8489	0.3104	3.8850	3.0296	0.1375	0.9291	1.3674	3.3955	2.3760	6.2061	3.8873
	N	8	8	10	10	11	9	7	11	10	10	11	9

S_G = Significant (S) or Not Significant (NS)
T = Paired T Test Value
N = Number of events

* Significant at 95% but not at 98%

TABLE C5

Variance Within Sampler Types

$\overline{U}.f \leq 11$ km/hr

		H_3O^+	NO_3^-	SO_4^{-2}	NH_4^+	Cl^-	F^-	Cond.	Ca^{+2}	Mg^{+2}	Na^+	K^+	R
A	S_G	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	T	1.2748	1.1841	.063395	.53936	.39101	.48038	1.3367	.66581	1.0502	.63246	.26069	.13383
	N	10		10	9	9	10	10	10	8	9	8	12
F	S_G	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	S
	T	1.9958	.99947	.38206	.78799	.41981	1.0038	1.1049	.07179	1.1286	.06835	.96684	2.6936
	N	12	11	12	11	8	12	12	12	11	12	13	14
S	S_G	S	NS		NS	NS	NS	NS	NS	NS	NS	NS	NS
	T	2.2922	.18130	.03158	.26872	1.10987	.63671	1.5845	.70900	.56000	.26743	.20082	.35759
	N	10	11	12	12	8	11	12	12	11	12	11	14

S = Significant (S) or Not Significant (NS) at 95%
T = Paired T Test Value
N = Number of Events

*NS at 98%

TABLE C6

Variance Between Sampler Types

Product $\overline{U} \cdot \overline{f} \leq 11$ km/hr

		NH_4^+	K^+	Na^+	Ca^{+2}	Mg^{+2}	Cl^-	Cond.	F^-	H^+	NO_3^-	R	SO_4^{-2}
A & F	S_G	S	S	S	S	S	S*	NS	S*	NS	S	NS	S
	T	2.8623	.6063	4.7775	4.2890	3.8444	2.5485	0.3273	2.2985	1.7566	4.3817	1.1976	5.0579
	N	11	11	13	14	14	11	14	14	12	13	15	11
A & S	S_G	NS	NS	NS	NS	S	S*	NS	S*	NS	S	S	NS
	T	0.4240	1.5018	1.3834	2.0714	3.2240	2.3763	0.9137	2.4922	2.0000	2.7083	4.6922	1.4002
	N	11	11	13	14	14	10	14	14	12	13	15	11

S_G = Significant (S) or Not Significant (NS)
T = Paired T Test Value
N = Number of Events

* Significant at 95% but not at 98%

TABLE C7

Variance Within Sampler Type

$\overline{U}.f > 11$ km/hr

		H_3O^+	NO_3^-	SO_4^{-2}	NH_4^+	Cl^-	F^-	Cond.	Ca^{+2}	Mg^{+2}	Na^+	K^+	R
A	S_G	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	T	.73835	.21494	1.34388	.73490	.24977	.98308	.43571	.50230	.60302	1.0286	1.1857	1.1343
	N	13	12	10	10	10	10	7	9	7	9	9	10
F	S_G	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	T	.37717	2.5535	1.55080	1.3721	1.1708	.14415	.09657	1.7147	.34563	.91848	1.1795	.85066
	N	14	13	13	12	12	13	12	13	14	11	9	11
S	S_G	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	T	1.0567	.82589	.17915	.11128	.48551	.69033	.86830	.52426	.85679	.84020	.87344	1.0000
	N	15	13	13	11	12	13	14	13	14	11	8	12

S = Significant (S) or Not Significant (NS) at 95%
T = Paired T Test Value
N = Number of Events

*NS at 98%

TABLE C8

Variance Between Sampler Types

Product $\overline{U}.f$ > 11 km/hr

		NH_4^+	K^+	Na^+	Ca^{+2}	Mg^{+2}	Cl^-	Cond.	F^-	H^+	NO_3^-	R	SO_4^{-2}
A & F	S_G	S	S*	NS	S	S	NS	NS	NS	S*	S	NS	S
	T	2.8449	2.9332	0.9995	3.3829	2.8250	0.9722	0.4801	1.6131	2.6106	3.4526	0.4541	3.3920
	N	9	8	10	10	10	9	6	9	10	10	11	9
A & S	S_G	NS	S*	NS	S	S*	NS	NS	NS	S	S	NS	S
	T	1.2776	2.8089	0.0397	3.4679	2.5808	0.1064	0.1006	0.8903	2.9933	3.4084	0.7712	4.4524
	N	8	8	10	9	10	9	6	9	10	10	11	9

S_G = Significant (S) or Not Significant (NS)
T = Paired T Test Value
N = Number of Events

* Significant at 95% but not at 98%

TABLE C10

Variance Between Sampler Types

Rainfall > 5 mm

		NH_4^+	K^+	Na^+	Ca^{+2}	Mg^{+2}	Cl^-	Cond.	F^-	H^+	NO_3^-	R	SO_4^-
A & F	S_G	NS	S	S	S	S	NS	NS	NS	NS	NS	NS	S
	T	0.8327	2.531	2.980	3.7118	3.1409	2.0639	1.0167	1.5992	2.2091	1.3774	0.7331	4.9996
	N	10	10	12	12	12	10	12	11	10	12	12	10
A & S	S_G	NS	NS	NS	S	S	NS	NS	NS	NS	S	NS	S
	T	0.1947	0.5346	1.9725	3.0493	2.5697	1.7580	1.1847	0.4198	0.1715	2.5031	0.5253	0.7461
	N	10	10	12	12	12	9	12	11	10	12	12	10

S_G = Significant (S) or Not Significant (NS)
T = Paired T Test Value
N = Number of Events